



NANOTECHNOLOGY (MATERIALS AND APPLICATIONS)

Editor

DR. M. R. JAYAPAL

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Dr. M. R. Jayapal

Senior Scientist,
Department of Chemistry and Materials Science Engineering,
Yancheng Institute of Technology, China.

Kripa-Drishti Publications, Pune.

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Editor: Dr. M. R. Jayapal

Authored by: Rajabhuvaneswari Ariyamuthu, Valentine Rupa, Sangeetha Je., Dr. Ajay Kr. Thakur, Kirubanandan Shanmugam, Manish Kumar, Preetismita Borah, Dr. D. Prakash, Priyanka Nayar, Pooja Yadav, Paresh Nageshwar, Upendra Singh, Anupam Agnihotri, Melita Menelaou, Dr. Sanjeeb Sutradhar, Dr. Soumyakanta Prusty, M. S. Shabana, C. Rangunath, Dr. V. Ramasubramanian, Shalini, Prerna Verma, Prof. Tanmay Ghosh, Dr. Padmakar G. Chavan, G. V. S. Subbaroy Sarma, M. Jemimah Carmichael, Murthy Chavali

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PREFACE

Compared with conventional technologies and sciences, the development of nanoscience and nanotechnology dealing with the synthesis and characterization of nanostructure materials has been quite rapid and intensive, while also unprecedented. Now the technologies based on nanoscience and nanotechnology are exerting a profound and strong impact on every field of conventional technology and science.

In fact, all different scientific disciplines, including every single sector (such as nanomaterials, micro and nanomachines, micro and nanoelectronics), have their own paradigm. This is why innovations and industrial developments are profoundly different. However, these fields are strongly interlinked. It is therefore necessary to make our studies more interdisciplinary in order to enable us to understand the nanoworld.

Nano sciences and nanotechnologies are leading to a major turning point in our understanding of nature. Such a force has its consequences or in the words of a famous fictional character: every force has its dark side. Our future depends on how we use new discoveries and what risks they bring upon humanity and our natural environment. The ethical implications of this must therefore be discussed.

This book presents the possible applications of nano-sized materials in environmental processes. It is by far the most reliable guideline for the selection of nanomaterials to improve the efficiency of environmental processes and for designing nanomaterials for specific environmental processes and pollutants. The impact of nanomaterials on the environment has also been discussed in the book to help avoid causing secondary contamination by use of nanomaterials and to provide proper information about nanomaterials to potential users who wish to use and apply them in environmental technology.

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1. An Introductory Approach to Composite Materials

Rajabhuvaneswari Ariyamuthu

Sri Sairam Institute of Technology,
Development of Chemistry,
Chennai.

Valentine Rupa

Assistant Professor,
Department of Chemistry,
Salem Government College,
Salem.

Sangeetha Je.

Assistant Professor,
Department of Chemistry,
American College,
Madurai.

Abstract:

Even though people have been using composite materials for millennia, the notion of composites as a distinct material classification was not recognized until the mid-twentieth century. Composite materials are made up of two or more different material phases. The ancient Mesopotamians may have been the first to understand that bonding wood at an angle generated superior qualities to single-ply wood.[1.1]. Composites are frequently stronger, have a lower density, and are less expensive than traditional materials. Composites are typically made up of two or more separate components that constitute big enough regions to be called continua; the basic components are usually tightly fused at the interface. A composite material is a mixture of two or more materials with chemical and physical properties that differ. They are designed to work together to achieve a certain goal, such as boosting strength, reducing weight, enhancing electrical resistance, and so on. The various systems are judiciously combined to achieve a system with more useful structural or functional properties qualities that none of the constituents could achieve on its own. Low weight, corrosion resistance, good fatigue strength, and speedier assembly are just a few of the benefits. They're widely employed in airplane structures and electrical components, packaging medical devices, and from spacecraft to home construction [1].

Keywords:

Dispersed phase, Matrix phase, corrosion resistance, Mechanical strength

1.1 Introduction:

Composites are made up of different materials with different compositions, yet the individual constituents retain their identities. These individual constituents work together to provide the composite item with the required mechanical strength or stiffness. A composite material is made up of two or more separate phases (matrix and dispersion) and has bulk properties that are notably different from those of the constituents. The fundamental phase with a continuous feature is the matrix phase. The matrix phase is typically more ductile and less rigid. It is responsible for holding the scattered phase and sharing a burden with it. In a discontinuous form, the dispersed (reinforcing) phase is embedded in the matrix. This secondary phase is called the dispersed phase. Because the dispersed phase is frequently stronger than the matrix, it is occasionally used.

composition materials" or simply "composites" as the most commonly used word are materials made up of two or more components that have significantly different physical and/or chemical properties. When two or more fundamental components are combined, a new substance emerges with properties distinct from the individual constituents. Composites must be distinguished from material mixtures and solids solutions because the individual components stay unique and independent within the final material structure.

Individual basic ingredients, referred to as constituent materials, are used to make composite materials. The matrix and the reinforcement are the two primary types of component materials. To make a composite, at least one representative from each category is required. By retaining the reinforcements' relative placements, the matrix phase embeds, surrounds, and supports them. The reinforcements offer their unique physical and mechanical qualities to the matrix, improving its properties.

The acquired synergism between the two phases creates material qualities not seen in the individual constituent materials, while the designer can construct ideal combinations of binders and reinforcements, resulting in tailor-made composites [2]. Composite materials have swooped in and shown enormous potential in integrating a variety of industrial and manufacturing industries. A matrix is a mesh made up of readily available materials such as glass fiber, carbon fiber, and polymers. Other materials, such as nanoparticles and graphene, are also commonly employed in matrices. [1.2]

The following are some well-known composite materials:

- a. In sludge, lignocellulosic (straw)
- b. The material is wood (cellulose fibers embedded in hemicellulose and the binder lignin)
- c. skeletons (soft protein collagen combined with the hard mineral apatite)
- d. [3, 4] Pearlite (ferrite and cementite mixed)

1.2 The Fundamentals of Composites:

By definition, composite materials are made up of at least two different materials. Each takes on a different phase in a combination, such as a matrix phase or the dispersion phase.

1.2.1 Matrix Phase:

The matrix is the basic phase having a continuous character. It maintains the scattered phase together by sharing a load with it. In many cases, the matrix is more malleable and ductile. Matrix is the fundamental phase, which has a continuous character. The matrix phase is typically more ductile and less rigid. It is responsible for holding the scattered phase and sharing a burden with it.

1.2.2 Dispersion Phase:(Reinforcing):

The dispersed phase is a second phase that is embedded in the matrix in a discontinuous form. It is known as the reinforcing phase because it is often stronger than the matrix. [1.2]

The second phase (or phases) is a discontinuous shape incorporated into the matrix. The dispersed phase is usually stronger than the matrix, it is also known as the reinforcing phase.

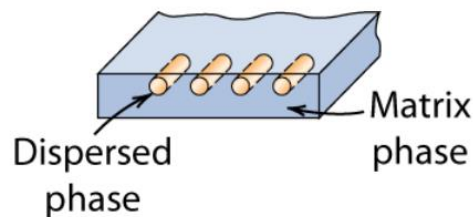


Figure 1.1: Different Phases of Composites

Composite materials are divided into two classification systems. One is based on the matrix material (metal, ceramic, or polymer), while the other is based on material structure:

1.3 Composites I: Classification (Based on Matrix Material):

a. Metal Matrix Composites (MMC):

Metal matrix composites (MMCs) are composites in which the matrix phase is a metal, such as aluminum, magnesium, titanium, or other metals. Because of the high density of metals, metal matrix composites are less popular than polymer matrix composites (PMC). Metals, on the other hand, have greater strength and stiffness than polymeric materials and can resist higher temperatures. A scattered ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase is mixed with a metallic matrix. For structural applications, a lighter metal such as aluminum, magnesium, or titanium is preferred. This gives the reinforcement and the structure as a whole support. [1.2]

b. Ceramic Matrix Composites (CMC):

Ceramic Matrix Composites are made up of a ceramic matrix with other ceramic fibers implanted in it (dispersed phase). Ceramic is a key ingredient of ceramic matrix composites

where metal or other inorganic materials are employed as reinforcement. Ceramics have a high melting point temperature, great compressive strength, good strength at high temperatures, and good oxidation resistance. Ceramics, on the other hand, have low tensile and impact strength, both of which can be enhanced by using appropriate reinforcing elements.

Ceramic fibers are incorporated in a ceramic matrix phase in this type of composite. This sort of structure solves the problem of low crack resistance that plagues traditional ceramic structures. Carbon, Silicon Carbide, Alumina, and other materials are excellent choices for both the matrix and scattered phases. The shaft sleeves for large pumps shown below were made utilizing SiC-fibre reinforced SiC material and chemical vapor infiltration. [1.2]

c. Polymer Matrix Composites (PMC):

Polymer is employed as the matrix phase in polymer matrix composites, whereas organic, inorganic, or hybrid materials are used as the reinforcing phase. Polymer matrix composites provide several advantages over metal and ceramic matrix composites, including low density, high extensibility, high shock absorption capability, inexpensive fabrication costs, and so on. As a result, polymer matrix composites outnumber metal and ceramic matrix composites in popularity. Metal matrix composites, on the other hand, are commonly utilized over PMC when high service temperatures and strength are required. Currently, fiber-reinforced polymer composites account for more than 90% of all composites.

Glass, carbon, steel, or Kevlar fibers are incorporated in a thermoset (Unsaturated Polyester (UP), Epoxy (EP)) or thermoplastic (Polycarbonate (PC), Polyvinylchloride, Nylon, Polystyrene) matrix (dispersed phase). Polymer matrices glue together various short or continuous fibers in this form of composite. The most common matrices are thermoset resin systems such as epoxies, phenolics, and polyamides. The lightweight, high rigidity, and high strength of PMCs are well-known. [1.2]. These polymers are good matrix materials since they're easy to work with, have a low density, and have desirable mechanical properties. As a result, high-temperature-resistant polymeric resins are commonly employed in the aerospace industry [6].

Thermosets and thermoplastics are two forms of polymers that are commonly used. Thermosets have a well-bonded 3D-molecular structure that develops after curing. At high temperatures, these materials disintegrate rather than melt. To adjust the curing conditions and decide on other qualities, simply changing the resin's fundamental composition is sufficient. They can also be kept partially cured for long periods. Furthermore, thermosets have a great degree of flexibility. As a result, they're ideal as a matrix basis for FRC in advanced applications. Thermosets are commonly employed to make chopped fiber composites, particularly when starting with a premixed or molded compound containing fibers of a given quality and aspect ratio, as is the case with epoxy, polymer, and phenolic polyamide resins. Thermoplastics are materials with a one- or two-dimensional molecular structure that melt at high temperatures and have exaggerated melting points. Additionally, their softening at high temperatures is reversible; hence, their original properties may be recovered by cooling, making it easier to apply proven compression procedures to make molded composites.



Figure 1.2: Polymer Matrix Composites

1.4 Composite Material Classification II (Based on Reinforcing Material Structure):

Fibrous, particulate, and laminate composites are the three types of composites based on reinforcement.

a. Composites of Particulate Matter:

Particulate composites are made up of flakes or powdered particles that are spread or implanted in a binding matrix. Concrete and wood particle boards are well-known examples of this type [5].

Particulate Composites are made up of a matrix that is reinforced by a dispersed phase that takes the shape of particles. Particle-reinforced composites. Particulate Composites are made up of a matrix that is reinforced by a dispersed phase that takes the shape of particles. Particles are randomly oriented in composites. These materials' dispersed phase is made up of two-dimensional flat platelets (flakes) that are laid parallel to one other.

- Particle-reinforced composites are composites that have been reinforced with particles.
- Due to their ease of availability and low cost, these are one of the most extensively utilized types of composite constructions. They can be further divided into two types based on the process of strengthening: particulate and dispersion-strengthened.
- The particles in this scenario are much smaller, ranging from 0.01 to 0.1 μm in size. Similar to precipitation hardening in metals, the strengthening happens at the atomic and molecule level.
- Examples: High-temperature strength is provided by Thoria (ThO_2) distributed Nickel alloys. Sintered Aluminium Powder (SAP) is a type of alumina powder that is distributed on an aluminum matrix.

This type of composite comprises a high proportion of coarse particles. Rather than necessarily improving qualities, they are frequently meant to develop unique combinations of them. They work with all three types of matrices: MMC, CMC, and PMC.

Examples: Power-cutting tools are made from tungsten carbide or titanium carbide embedded with cobalt or nickel.

b. Fiber-Reinforced Composites:

Fibrous Composites with a dispersed phase of fibers improve strength, stiffness, and fracture resistance. The material's toughness prevents crack propagation in directions parallel to the fiber. When fibers are placed in a specific direction (preferred orientation) and force is applied in the same direction, the strength increase becomes considerably more significant.

Long-fiber (continuous-fiber) reinforced composites have a stronger effect than short-fiber (discontinuous-fiber) reinforced composites. Short-fiber reinforced composites have a restricted ability to transfer load since they are made up of a matrix reinforced with a dispersed phase in the form of discontinuous fibers.

The dispersed phase - fibers - carries the majority of the load imparted to a long-fiber reinforced composite. In such materials, the matrix only acts as a binder for the fibers, holding them in place and protecting them from mechanical and chemical harm.

The mechanical qualities of fiber-reinforced composites, such as strength and strength-to-weight ratio, are increased. It is made up of strong, stiff, but brittle fibers that are embedded in a softer, ductile matrix. The matrix serves as a conduit for the load to be transferred to the fibers that do the majority of the heavy lifting.

- They're further divided into two types: continuous and discontinuous fibers.
- The length of the fibers in continuous fiber composites can range from a few feet to several thousand feet. Important design requirements can be strengthened and adjusted by enabling a uniform orientation of the raw composite fiber.
- Continuous fiber composites are generally more expensive than their discontinuous fiber counterparts. However, it compensates for this by greatly improving performance.
- Fiber-reinforced composites with discontinuous fibers
- This composites sub-division is further subdivided into two sub-sub-divisions. Discontinuous aligned fibers and discontinuous randomly oriented fibers are the two types of fibers.
- Shorter lengths of extremely condensed fibers aligned in one definite orientation in a matrix make up discontinuous aligned fiber composites. They have mechanical properties that are comparable to those of continuous fiber composites that are unidirectional. However, the shorter fibers reduce the composite's ductility, making it excellent for high-strength, low-ductility applications.

Short, condensed fibers implanted in all directions of a matrix make up discontinuous randomly-aligned fiber composites. Aligned fiber composites offer improved mechanical properties solely in the reinforcement direction. By randomly embedding the fibers in all directions of the matrix, this anisotropy can be avoided. While this may result in a reduction in peak strength, it does so at a lower cost by increasing formability.

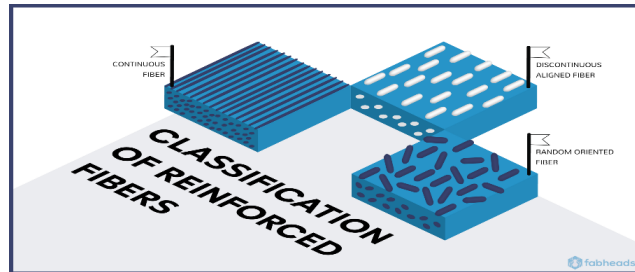


Figure 1.3: Alignment of Reinforced Fibers

c. Composite Laminates:

Laminar composites and sandwich composites are two types of structural composites that are commonly employed. Structural composites are a subset of composites. Their qualities are influenced by the geometrical design of various structural elements as well as the constituents' properties. Two-dimensional sheets/layers with a chosen strength direction make up laminar composites. These layers are stacked and bonded together based on specific requirements. In a plastic matrix, materials such as metal sheets, cotton, paper, and woven glass or carbon fibers are incorporated. Layers with varied anisotropic orientations or a matrix reinforced with a dispersed phase in the form of sheets make up laminate composites. In two directions, laminate composites provide improved mechanical strength, but only in one direction, perpendicular to the desired orientations of the fibers or sheet, the material's mechanical characteristics are low. Laminar composites include thin coatings, heavier protective coatings, claddings, bimetallic, and laminate. Sandwich structures are made up of thin layers of face material that are linked to a lightweight filler core. The core separates the faces and provides shear rigidity along planes perpendicular to the faces, resisting deformations.

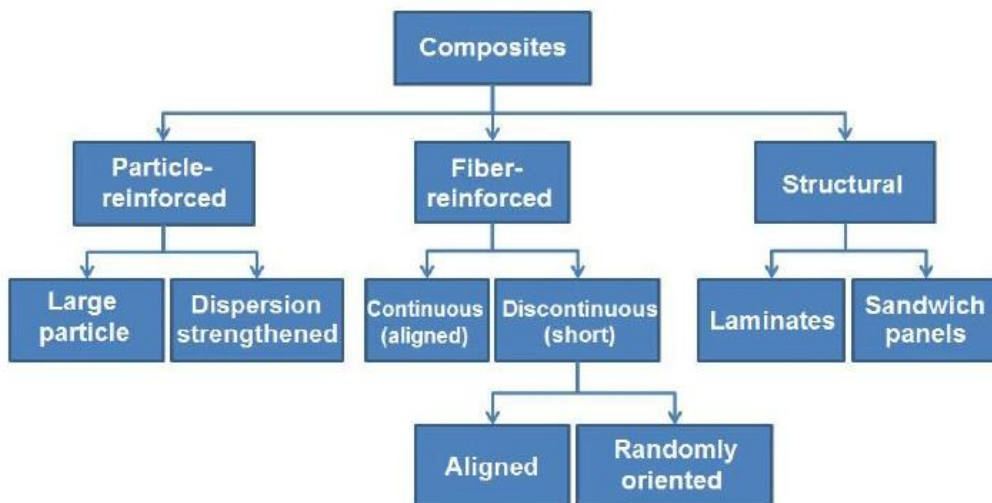


Figure 1.4: Classification of Composites Based on Fiber Reinforcement

1.5 Characteristics of Composites:

We already know that there are many different types of composites based on the classification of these materials. It's a well-known fact that different types of composites operate differently. Composites, on the other hand, share some features. Polymer matrix composites have emerged as the most rapidly emerging and widely used composites due to their inherent advantageous properties. In comparison to well-known materials such as metals, polymer matrix composites have the following characteristics:

1.5.1 Specific Strength and Modulus Are Both High:

The high specific strength and specific modulus of polymer matrix composites are the most essential advantages. The ratio of strength to density is defined as a specific strength, while the ratio of modulus to density is defined as a specific modulus; in both situations, length is the appropriate dimension/unit. These metrics, which are particularly important for aerospace structural materials, are tools to quantify the material's bearing capacity and stiffness capabilities under the premise of equal mass.

The great performance and low density of reinforcing fibers can explain composites' high specific strength and specific modulus. The specific modulus of glass fiber resin matrix composites is slightly lower than that of metallic materials due to the low modulus and high density of glass fibers.

1.5.2 Good Damping Characteristics:

The natural vibration frequency of forced structures is proportional to the square root of the specific modulus of structural materials and is related to the geometry of the structure. As a result, composites have a high inherent frequency, making resonance creation difficult in general. Simultaneously, the fiber/matrix interface in composites absorbs vibrational energy very quickly, resulting in significant vibration damping of these materials. Vibrations can be quickly stopped if they occur [10].

1.5.3 Composites – Fabrication:

Wetting and mixing the reinforcement with the matrix is a common step in the fabrication of composite materials. After that, a heat or chemical process binds them together forming a hard structure. Preset molds are created based on a variety of factors such as the materials used, the order and method of material introduction, the required elements, and so on.

It can be accomplished using a variety of methods including

- Spray Lay-Up
- Wet/Hand Lay-up
- Vacuum Bagging
- Filament Winding
- Pultrusion
- Resin Transfer Moulding (RTM)

- Autoclave Curing
- Resin Film Infusion (RFI)
- Chemical vapor deposition
- Centrifugal Casting

1.6 Applications of Composites:

Resins bonded with thermoplastics are currently a rapidly growing class of composites. Many research and development efforts in this area are now focused on enhancing the fundamental properties of resins and deriving the maximum potential functional advantages from them for specific applications.

This includes efforts to use precarious metals as a substitute in die-casting operations. The previous few decades have seen a significant shift in how people think about technology. With each passing day, the number of applications appears to grow exponentially.

The number of uses for composites has increased as the market and manufacturing methods have advanced. Aerospace, drones, construction, corrosion-resistant equipment, consumer products, antenna structures, radar, rocket engines, satellite structures, solar reflectors, and other spacecraft and other industries are among them.

- **Aircraft:**

Rotor shafts in helicopters, compressor blades, engine bay doors, fan blades, flywheels, helicopter transmission structures, jet engines, turbine blades, turbine shafts, wing box structures, and so on.

- **Aerospace:**

If one wishes to dominate the aerospace business, the lightweight and high specific strength is a big asset. Composite materials fit like a glove when it comes to properties like fatigue and corrosion resistance, a higher degree of optimization, and the possibility of cost savings.

The graphic above shows the overall material composition of a standard Airbus 350. Composite materials account for 53% of the total materials used.

- **Drones:**

Drones have found applications in everything from surveillance to food delivery, photography, and surveillance in just a few years. The drone's cargo has a significant impact on flight time and battery consumption. Composite materials play an important part in the design and manufacture of drones to reduce their weight. They can replace traditional materials such as aluminum, which is a good option for drone production but adds to the total weight.



Figure 1.5: Applications of Composites

- **Automobiles:**

Abrasive materials, bearing materials, electrical machinery, engine parts such as bearing materials, connecting rods, crankshafts, cylinders, pistons, and so on, pressure containers, truss members, cutting tools, electrical brushes, and so forth.

Wind turbine blades: carbon-wood epoxy composite wind turbine blades.

Tungsten carbide (WC), titanium carbide (TiC), and chromium carbide are the most common cemented carbides (Cr_3C_2) that can be used.

Cutting tools are the most common application for tungsten carbide cermets and other applications include powder metallurgy dies, indenters for hardness testers, wire drawing dies, rock drilling bits, and other mining tools.

Titanium carbide cermets (Ni-binder) are used in high-temperature applications such as gas turbine nozzle vanes, steel cutting tools, valve seats, thermocouple protection tubes, and torch tips.

- **Construction:**

For a long time, composite materials have found a place in the civil and construction industries. Cladding, drywalls, furnishings, building cores, and foundations have all benefited from composite material's adaptability. High tensile strength, fatigue resistance, low bulk, and other properties of fiber-reinforced plastic composites are suitable for civil engineers. Floors, bearing pads, concrete structures infused with steel plates or bars in a sandwich structure, beams and bars, and wood panels are only a few examples of composite use in construction.

- **Sports:**

In the future, the composites have infiltrated almost every facet of life. Sports and recreation are intriguing areas where it has made a stronghold. From racing helmets to safety gear to tennis rackets and hockey sticks, there's something for everyone.

- **Consumer Appliances:**

Phones, home appliances, insulator boards, component systems, circuit breakers, lighting devices, insulated cables, and other electronic equipment all use composite materials in some way.

1.7 Conclusion:

This article provides a basic explanation of composite materials and the various types of composite materials that are categorized based on the specific features and characteristics of composite materials required in the end-use. The importance of composite materials and their use since ancient times underscores their value.

The composite sector is becoming increasingly profitable with each passing day. The worldwide composite market is growing at a rate of 5% per year, while carbon fiber demand is increasing at a rate of 12% per year. Composites have taken over the world, with uses ranging from aerospace and automotive to healthcare and electronics.

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2. A Study on Nanotechnology Applications and Physics

Dr. Ajay Kr. Thakur

Assistant Professor,
P. G. Dept. of Physics,
C. M. Science College,
Darbhanga, Bihar.

Abstract:

Many technology and industry areas, including information technology, energy, environmental research, medicine, homeland security, food safety, and transportation, are benefiting greatly from nanotechnology's innovations. If you think about it, today's nanotechnology is the result of all the development made in the fields of chemistry, physics, materials science, and biotechnology in recent years. Our world's environmental problems can be solved with nanotechnology since it has the potential to be cost-effective, ecologically friendly, and permanent. In recent years, there has been a steep increase in nanotechnology in the domains of medicine, particularly in the delivery of targeted drugs. Nanotechnology has the potential to address global challenges in (1) water purification, (2) clean energy technologies, (3) greenhouse gas management, (4) materials supply and usage, and (5) green manufacturing and chemistry.

In the field of food and agriculture, nanotechnology is being used to improve nutrient delivery, separate proteins via bio-separation, rapidly sample for biological and chemical pollutants, and nano-encapsulate nutraceuticals. In numerous technology and industry sectors, nanotechnology is helping to significantly improve or even revolutionise. These include information technology, energy and environmental science, medicine, homeland security, food safety, and transportation. New materials with unique features can be created using nanotechnology, which takes advantage of recent advancements in chemistry, physics, materials science, and biotechnology. As more and more Nano-engineered materials reach the global market, the ongoing revolution in nanotechnology will lead to the fabrication of nanomaterials with properties and functionalities that will have positive changes in the lives of our citizens, be it in health, the environment, electronics or any other field. Nanotechnology. When it comes to power generation, conventional fuel resources can no longer be the primary source of power because of rising demand and increased emissions of carbon dioxide. Energy sources based on cutting-edge technologies must be pushed as a means of cutting emissions. Innovations in organic photovoltaics and other nanostructured and composite solar cell systems, such as roll-to-roll manufacturing processes, hold considerable promise in terms of the technology's future growth and development.

Keywords:

Nanotechnology, Nanomaterial, drug delivery, Physics.

2.1 Introduction:

In nanoscience and nanotechnology, we study materials at the atomic and molecular levels, typically with structures smaller than 100 nm in diameter. "Nanoscience" can be characterized as a scientific study of phenomena and material manipulation at the atomic, molecular and macromolecular scales, where the properties differ from those at a larger scale, as well as novel functional applications. In the context of nanotechnology, this is the design, fabrication, and use of structures, devices, and systems by controlling the material's size and shape at a nanometer (10^{-9} of a meter). [1]

Richard Feynman's "There's Plenty of Room at the Bottom" lecture at a conference of the American Physical Society at Caltech on December 29, 1959, inspired the idea of nanotechnology, in which he believed that the complete Encyclopedia Britannica could sit in the head of a pin. Norio Taniguchi, a professor at Tokyo's Science University, first used the word "nanotechnology" in a 1974 paper to describe the processing, separation, consolidation, and deformation of materials down to the atoms or molecules scale. However, it wasn't until the 1980s when the scanning electron microscope was invented that nanotechnology began to gain traction. [2]

With the growing need to protect our environment, the challenge of satisfying the world's energy needs is exacerbated. Clean, inexpensive, and renewable energy sources are being investigated by many scientists, along with strategies for reducing energy consumption and the environmental toxin burden. Nanotechnology-enhanced prototype solar panels are more efficient at converting sunlight into electricity than normal designs, opening the door to more affordable solar power in the future. [3] When it comes to production and installation, nanostructured solar cells are already more cost-effective and easier to utilize because they can be manufactured in flexible rolls rather than single panels.

Figure 2.1 shows an example of a nanotechnology application.

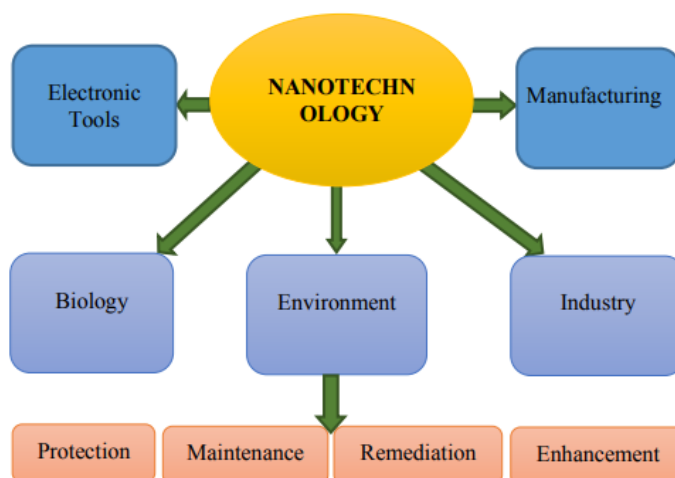


Figure 2.1: Application of Nanotechnology

Nanotechnology can be used in agriculture in different ways.

- Crop improvement
- Increase efficient fertilizers and pesticides
- Soil management.
- Plant disease detection.
- Water management
- Analysis of gene expression and Regulation
- Post-Harvest Technology

2.2 Nano Technological Applications in Food Industry:

Both developed and developing countries are investing in nanotechnology in an effort to get a foothold in the market. Nutraceuticals, gel and viscosifying agents, nutrient propagation, mineral and vitamin fortification, and nano-encapsulation of tastes are all examples of food processing techniques that incorporate the incorporation of nanomaterials into the process. [4]

2.3 Advantages and Disadvantages of Nanotechnology:

Even though nanotechnology is advancing in a number of fields, it is not without its drawbacks. It encourages the use of renewable power, extends the electronics limit, and helps in medical progress.

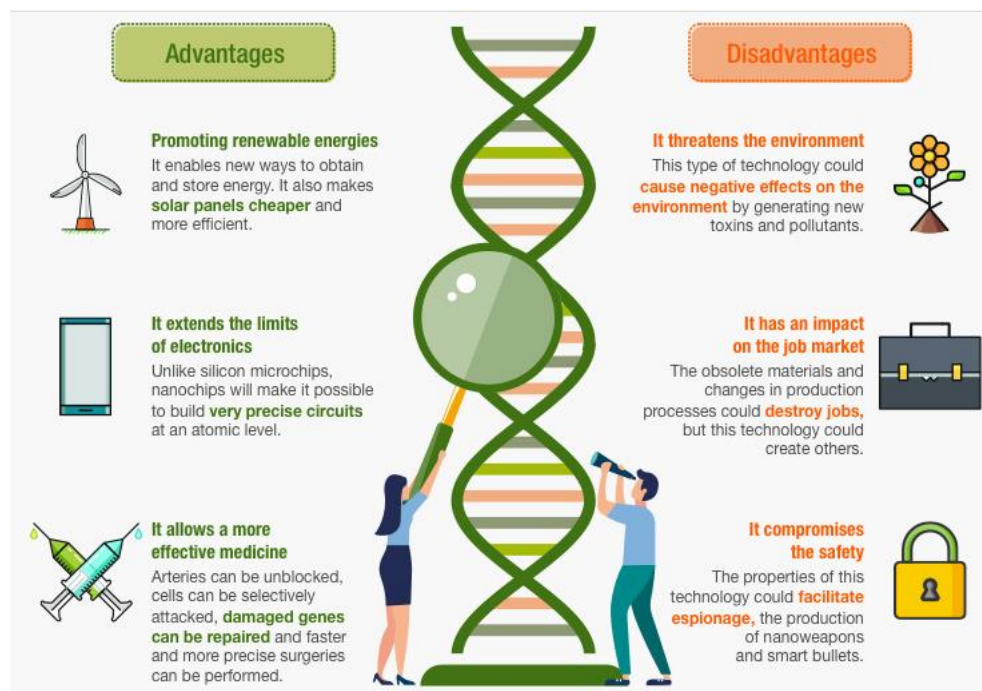


Figure 2.2: Advantages and Disadvantages of Nanotechnology

2.4 Review of Literature:

By modifying enzymes at the molecular level, researchers hope to speed up the conversion of wood chips, maize stalks (not only the kernels, as is the case today), and unfertilized perennial grasses into ethanol for use as fuel (Chaturvedi and Dave, 2014). [5]

In an effort to minimise the cost of fuel cells for alternative transportation, nanostructured materials are being researched to dramatically improve hydrogen membrane and storage materials and the catalysts required. Researchers are also striving to create a hydrogen fuel tank that is both safe and lightweight. A number of nanotechnology-based alternatives are being explored to transform waste heat from computers, autos, residences, and power plants into useful electrical power (Pratsinis, 2016; Sabet et al., 2016). [6]

Toxic organic compounds have been produced and put into the environment in recent decades such that they can be used either directly or indirectly for a long time. A few examples of these include pesticides, fuels, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) (Jones, 2007). [7]

The elimination of chemical contaminations from a polluted area is a vital stage in environmental remediation, according to Mahdavian (2010) [8]. There have been numerous investigations into the development of more effective materials for adsorbing a wide range of contaminants. It was common practice to employ montmorillonite and bentonites to absorb oil spills since they were thought to be the smallest particles and could hold large quantities of chemicals. In order to detect *Acidovorax avenae* subsp. *citrulli*, Zhao et al. (2011) [9] developed a quick and sensitive DNA strip sensor based on gold nanoparticle-labeled oligonucleotide probes. Qualitative and semi-quantitative results on the target DNA were achieved; the strip sensor's qualitative detection limit was 4 nM. Anti-counterfeiting Nano barcodes were designed by Oxonica Inc. (USA) for use with desserts or pellets and given via a modified microscope. The use of nano-biodegradable packaging is also on the rise. For food packaging and carry bags, bioplastics may be able to take the role of fossil fuel-based plastics thanks to the utilization of nanomaterials.

Organophosphates can also be detected in plants, fruits, and water using Nano sensors. There is a pressing need for extremely sensitive and selective analytical techniques for pesticide residue detection because of its water solubility, toxicity, and widespread use in agriculture (Valdés et al. 2009). [10]

Foods like wine, coffee, juice, and milk may all be analysed using Nano sensors. The sensors are built utilising layer-by-layer macromolecule ultra-thin films that have a 10,000-fold more surface area than the human tongue. Additional bacteria can be detected by attaching Nano sensors to packaging. Instead of sending the packed food to a lab for testing, the sensors can be used to detect variations in colour that indicate changes in food quality. Gastro sensors and thermometers, as well as nanoparticle-based sensors and array biosensors, are frequently seen in food packaging. Nanocantilevers and electronic noses are other examples of sensors that are commonly found in food packaging (Tang et al. 2009) [11]

2.5 Objectives:

- To learn about nanotechnology as a research topic
- To investigate the latest developments in nanoscience and nanotechnology across a range of scientific disciplines
- Nanotechnology in food management will be studied.
- To study the use of nanotechnology in industry

2.6 Research Methodology:

It is the systematic, theoretical investigation of the methods used in a particular field of study. It is the study of a field's corpus of methods and principles from a theoretical perspective. Parameters like paradigm, theoretical model and phases are typically included in this type of research.

Secondary sources must be thoroughly reviewed and analysed in order to use analytical and descriptive methods to the research. Close reading of a few secondary materials would be necessary to expand the textual analysis and provide additional insights.

2.7 Result and Discussion:

Nanofoods are products that were grown, processed, or packaged using nanotechnology or nanotech materials. [12]

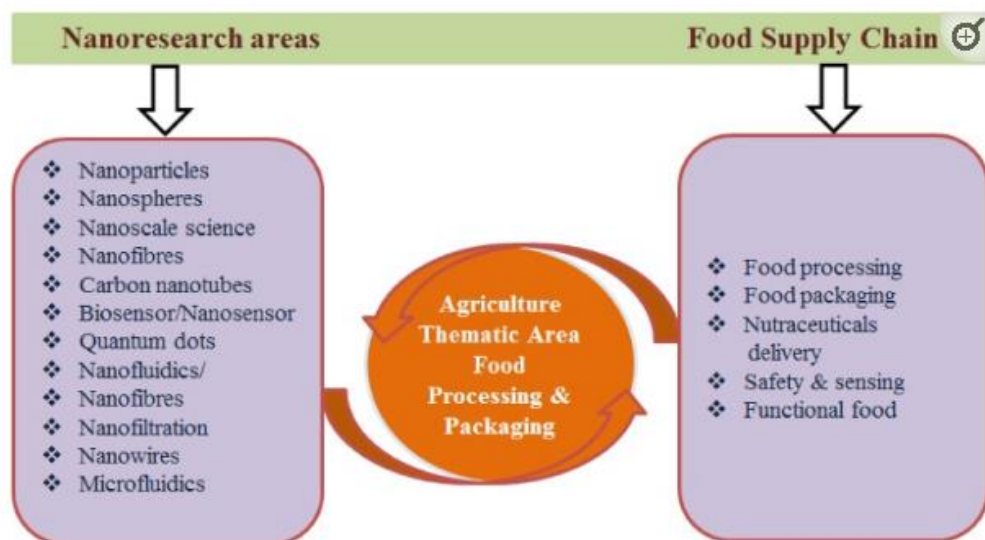


Figure 2.3: Framework for Integrating Nano Research Areas and the Food Supply Chain

Food processing, packing, and preservation require a number of procedures, all of which are aided by nanotechnology and a variety of nanomaterials. [13]

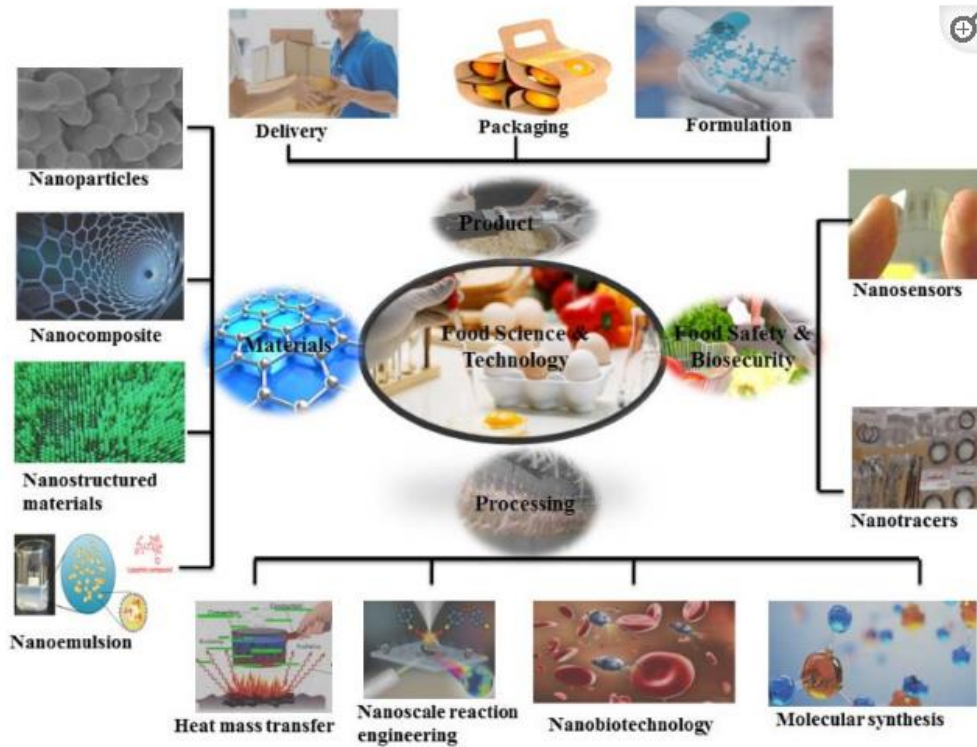


Figure 2.4: Food Management Steps

To study things down to the atomic scale in physics, chemistry, and computer science, nanoscience and nanotechnology have advanced in a variety of directions, allowing researchers to look at objects using a variety of microscopes, from room-sized computers to mobile slim laptops, and to study the nucleus of a cell in great detail in order to better understand single multicellular life. [14] Figure 2.5 summarizes all of these advancements in many branches of research in a general overview.

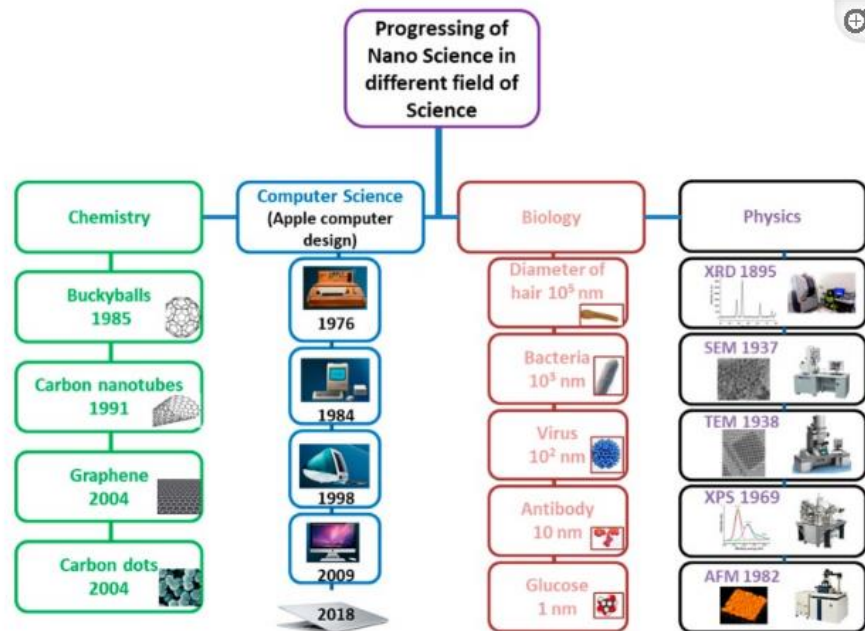


Figure 2.5: Progress in Nanoscience and Nanotechnology in Different Fields of Science.

Science and technology have long considered nanotechnology to be as transformative as the arrival of electricity or biotechnology or digital information. There was a 25 percent annual rise in discoveries, inventions, nanotechnology workers in R&D, funding programmes, and markets between 2001 and 2008. [15,17] In 2009, the global market for nanotechnology-based products totaled \$254 billion. The long-term outlook for 2000-2020 (solid line) and 2009 outcomes for the market of final products utilizing nanotechnology. The focus of R&D shifts from basic discoveries in the years 2000-2010 (Nano1 in the figure) to applications-driven fundamental and Nano system research in the years 2010-2020. (Nano2) [18]

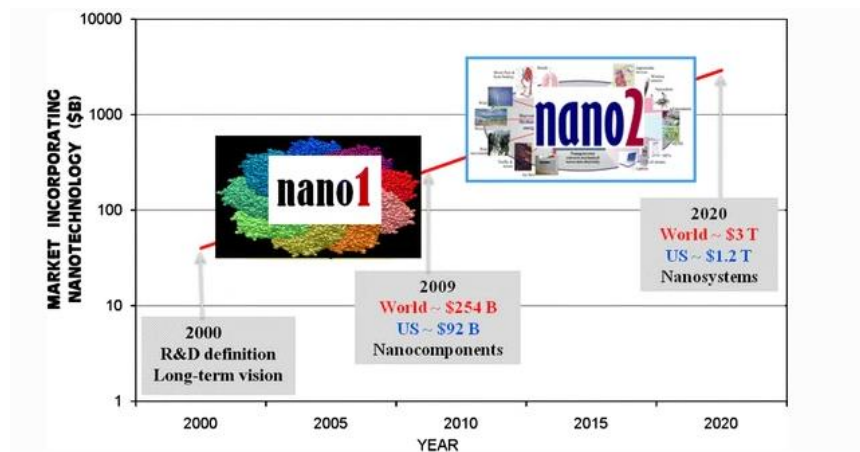


Figure 2.6: Nanotechnology Research Direction

2.8 Conclusion:

Building physically, chemically, and physiologically stable structures one atom or molecule at a time is the goal of nanotechnology, which takes an atomic or molecular approach. Astonishingly high levels of precision can now be achieved by manipulating individual atoms or molecules, thanks to advancements in science and technology. Even if nanotechnology's impact on society appears to be limited at the time, ongoing investment and labour are expected to yield results and innovations. The first step will be to improve food safety and quality. Finally, the use of nanotechnology in food processing can improve nutritional value while also ensuring product safety and promoting a healthy food culture. In the wake of biotechnology and information technology comes nanotechnology. The advancement of nanotechnology in aims to enhance the quality of life. As it continues to advance, nanotechnology will have a positive effect on both society and the environment.

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3. Development of Cellulose Nanofiber (CNF) Coating On (1) Metal Surface for free standing CNF Film and (2) Paper Substrates for CNF Barrier Laminates

Kirubanandan Shanmugam

Department of Biotechnology,
Sree Sastha Institute of Engineering and Technology
(Affiliated to Anna University, Chennai),
Chennai, India.

Abstract:

Paper is widely used in packaging applications and is biodegradable and therefore perfectly safe for the environment. The hydrophilic nature of cellulose limits the water vapour-barrier properties and oxygen barrier properties of paper. To mitigate these limitations, paper is often associated with other materials, such as plastics, wax and aluminum, for their good barrier properties. However, these materials suffer from serious environmental issues, as difficult and inefficient to recycle. Recently, cellulose nanofibers based materials has been considered as an alternative to produce eco-friendly barrier materials. Existing techniques to prepare cellulose nanofiber films/sheets/composites are commercially not feasible and expensive. Therefore, other cost effective and readily implementable methodologies are required to achieve cellulose nanofibers barrier layers. In the present thesis a novel approach is developed using spray coating technique to produce materials with excellent barrier properties. Among many coating techniques, the spray coating has many advantages such as the production of even coating surface on the base sheet and contactless coating with the substrate. A laboratory scale spray coating of cellulose nanofibers suspension on a paper substrate was developed. When the cellulose nanofibers suspension concentration was varied from 0.5 to 1.5 wt. %, coat weight is increased from 2.9 ± 0.7 to 29.3 ± 6.9 g/m². As a result, the air permeability of composite was decreased 0.78 ± 0.17 to < 0.0030 $\mu\text{m}^3/\text{Pa}\cdot\text{s}$. Scanning electron microscopy studies of spray coated paper confirms that the surface pores in the paper substrates are filled with sprayed cellulose nanofiber and forms a continuous film on the surface of the substrate. These are the probable reasons for the reduction of air permeability of composites. A rapid preparation technique to prepare free standing cellulose nanofiber films/sheets was also developed using a bench scale spray coating system. Cellulose nanofiber suspension with concentration ranging from 1 to 2 wt% was sprayed onto a stainless steel plate, which is moving on a conveyor at a velocity of 0.32 cm/sec and then air dried. The basis weight of produced cellulose nanofiber films is varied from 52.8 ± 7.4 to 193.1 ± 3.4 g/m². Processing time taken to prepare films was approximately 1.0 min, which is much less than processing times reported in the previous literature. Thus, the significant reduction in preparation time for producing the cellulose nanofiber sheet recommends that this spray coating technique can be utilized for the development of a scalable process for the fabrication of various cellulose based nanocomposite. Therefore, the laboratory scale spray coating

confirms that the spraying could provide a platform for development of films/sheets/nanocomposite and a barrier layers on the base sheet. The future work is the development of a continuous spray coating of cellulose nanofiber on the base sheet and evaluation of mechanical and barrier properties spray coated barrier layers on the base sheet.

Keywords:

Cellulose nanofiber (CNF), CNF Coating, Spraying, Free standing film, air permeability, tensile strength, uniformity.

3.1 Introduction:

Polymer based packaging materials are extensively used because of low oxygen and water permeability. However, they have poor recyclability and biodegradability and the waste is harmful to the environment. In conventional process, aluminum foil is used as layer for enhancing barrier properties of the paper board and paper surface.

Neither the plastic materials nor the aluminum are renewable and these composites are difficult to recycle. To resolve this problem for the food packaging materials after use, major efforts are being taken the way to identify alternative materials from natural source to improve the barrier performance as well as minimize disposal or recycle problems [1].

Cellulose nanofiber, also known as cellulose nano-fibres or nano-fibrillated cellulose, is made by breaking down cellulose fibres into fibres with diameters ranging from 4-100nm and is considered to be as building block for development of new cellulose based functional materials. Recently, cellulose fibrils are used in the development of high strength and barrier materials and nanocomposites [4].

The preparation of these materials generally based on filtration and dewatering of dilute cellulose nanofiber suspensions was investigated for the preparation of cellulose nanofiber sheet which has an excellent mechanical and barrier properties. Vacuum filtration has constraints for preparation of nanocomposite sheets as it required 1 to 24 hours of filtration time [5-7]. Recently, our group developed a technique to reduce the preparation time to 10 mins. [43]. However, this is still high enough to make scale up difficult [8].

Therefore, the rapid and flexible method for developing the cellulose nanofiber sheet is required. Cellulose nanofiber has a potential of renewable, recyclable, compostable and biodegradable alternatives to the synthetic polymer based products [2].

Cellulose nanofiber is used as coating materials for enhancing the barrier properties of a base sheet and fabrication of cellulose nanofiber sheet and films [3].

Spraying of cellulose nanofiber is an alternative technique for making nanofiber sheets that has been used to produce either continuous self-standing films by spraying on to a fabric or composite laminates by spraying onto a base sheet [6, 7].

Spraying has some significant advantages such as formation of homogeneous layer and contour coating on the substrates [7]. The range of basis weight achievable with spraying is much higher than has been obtainable with filtration.

Spraying can also be performed at higher initial solids content compared to filtration, reducing the amount of water that has to be removed in subsequent drying. Spraying has not so far been used to make discrete sheets for laboratory investigations, or for small scale products. It is still an open question about the sheet quality produced by spraying compared to hand sheets made by laboratory vacuum filtration.

The spray coating of cellulose nanofiber on the base surface could produce sheet with enhanced barrier and mechanical properties. Based on the laboratory performance of spray coating, the cellulose nanofiber sheet could be prepared rapidly and coating cellulose nanofiber on the base sheet quickly to create barrier layers.

The aim of this doctoral research is to develop spraying as a rapid and flexible method to prepare both free-standing cellulose sheet and to coat cellulose nanofiber on the base sheet. This report consists of the review of the literature of cellulose nanofiber, barrier layers and the spraying process, a review of the work done so far and a detailed research plan.

This research has broadly three main objectives.

- a. To make free standing cellulose nanofiber film/sheet by spraying, determining the range or properties achievable
- b. To develop spray coating of cellulose nanofiber on the base sheet to create barrier layers on a base sheet in a continuous mode and to determine the performance

3.2 Background:

3.2.1 Cellulose Nanofiber:

Cellulose is the most important bio-renewable, biodegradable and biopolymer available in nature and is an excellent feedstock for the development of various sustainable functional materials such as coatings, films and membranes on an industrial scale for production [9]. These bio-based products could provide an outstanding solution to various international problems such as recycling, disposal and incineration of waste. It is produced by disintegration and delamination of cellulose fibrils from pulp produced from a variety of green sources such as wood, potato tuber, hemp and flax. It has dimension diameter ranging from 5 to 100 nm and is typically several micrometers in length [10].

Moreover, having a smaller dimension and a larger surface, nano cellulose is a great opportunity to be developed more functional materials for various applications [11, 12]. These Cellulose fibrils at micro/nano scale are used to functionalize base sheets by coating or to make freestanding sheets/films and nanocomposites. [13]

The nomenclature for cellulose nanofiber has not been reported in a consistent manner in the previous scientific investigations. It is also called as micro fibrillated cellulose (CNF), nano-fibrils, micro-fibrils and nano-fibrillated cellulose (NFC). Nano-cellulose fibres are isolated and processed from wood via various chemical, enzymatic, and/or mechanical treatment.

Due to nano size of fibres, it possesses various outstanding properties, such as high aspect ratio, high specific strength, flexibility, large specific surface area, and thermal stability, combined with biodegradability and biocompatibility.

These properties could make cellulose nanofiber suitable for a wide range of applications, such as cellulose nanofiber film [14], reinforcing phase in composite materials [15], barriers in packaging [16], rheology modifiers for suspensions [17], filters for virus removal and water treatment technologies [18,19], flexible platforms for biomedical applications [20] and printed electronic applications [21].

3.2.2 Cellulose Nanofiber and Barrier Properties:

It has been proved that the films/sheets and its nano composites made from cellulose nanofiber and coated with fibre substrates increased the barrier and mechanical properties. [22].

Due to outstanding multifunctional barrier properties such as oxygen and water transfer rate, it has the potential for application of packaging materials for foods. [23]

3.2.3 Conventional Methods for Producing Barrier Surface on the Base Sheet:

Barrier materials required low gas and water permeability to protect the contents from the external influences and to preserve the flavour and nature of the packaged product. The barrier properties of paper-based packaging can be tailored by applying layer of either synthetic or natural polymer using coating process.

The previous studies confirmed that cellulose based coating on the paper based substrates substantially improved their barrier and surface properties. [24, 25] The various coating process using cellulose nanofiber from the literature were reported in the Table.1.

The cellulose nanofiber could be applied either on the paper or paperboard by several techniques such as solvent casting, dispersion coating, foam coating, bar and blade coating, and vacuum filtration. The different coating processes are mentioned in Figure 3.1 and Table 3.1.

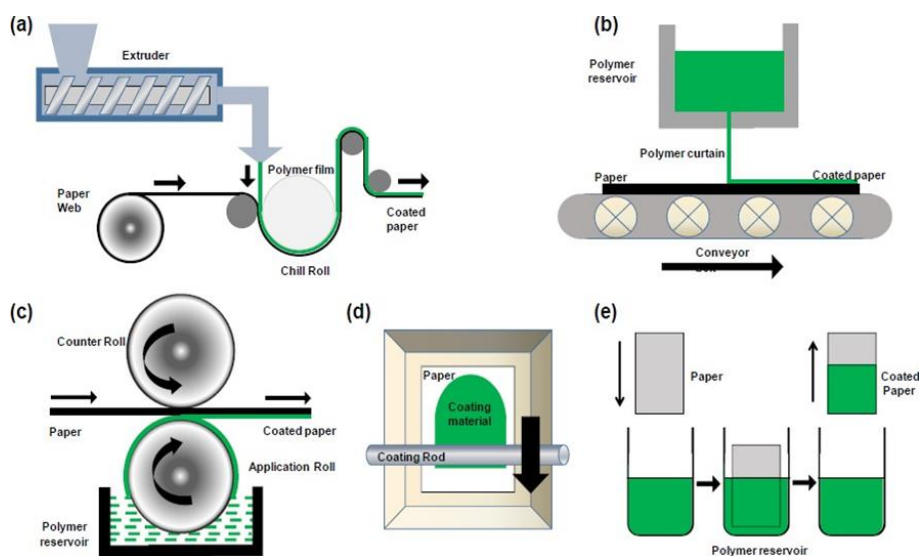


Figure 3.1: Different coating processes for paper applications, (a) extrusion coating; (b) curtain coating; (c) size press coating; (d) bar coating; and (e) dip coating. (Vibhore Kumar Rastogi *et al.*, *Coatings*, 2015, 5, 887-930)

Extrusion coating method is a common technique for coating synthetic polymers, such as poly-ethylene. It provides a continuous processing, uniform coating, minimal pinholes and cracks in the surface of base sheet, and solvent-free application. However, it has shortcomings in the coating performance such as being unable to produce a high coat weight to achieve the necessary barrier properties, instability of the polymer during melting stage and coating speed and efficiency. It is only suitable for coating of thermoplastic polymers. Given that cellulose nanofiber is not thermoplastic it can only be suitable as a coating formulation by either dissolving cellulose nanofiber in a suitable solvent (*i.e.*, solvent coating/casting), or dispersing the polymer in solvent (*i.e.*, dispersion coating). [26, 27]

In dispersion and solvent coating methods, low coat weights around 10g/m^2 can be used to achieve the barrier layers of the base sheet, but sometimes two layers are mandatory to coat to eliminate the surface pinholes and achieve a sufficient water vapour performance. In this case, post coating process is expensive process including evaporation and drying of the coated surface [1]. Aulin *et. al.* reported that the preparation of carboxymethylated microfibrillated cellulose (CNF) films by dispersion-casting from aqueous dispersions and by surface coating on base papers and confirming that the oxygen permeability of the sheet prepared via dispersion coating and air permeability were reduced. [22]

Curtain coating is where a uniform coating is applied and found sufficient to cover the entire surface with better gas and water vapour barrier properties. In size pressing, the coating is not covering the paper surface completely and does not provide expected barrier properties. Bar Coating and rod coating techniques provides a better control over the thickness of the coating layer, but can only be used at the laboratory or pilot scale [28]. Dip Coating is the quick testing performance of coating at laboratory scale. However, the coating thickness of the base sheet is difficult to control and hence always find practical application at the

laboratory scale [1]. Vacuum Filtration is the most common method for making the sheet. Time required to prepare sheets is varied to 10 min to 4 hours. This method achieves excellent barrier and mechanical properties, but preparation time is a bottle neck for scaling up the process. Due to its film forming capacity, cellulose nanofiber could be used as coating layer on the base sheet which enhances strength and barrier functions of the base sheet. It proved that cellulose nanofiber would be a potential coating material [1]. Size press is not able to significantly alter papers properties as the CNF coat weight barely reached 4 g/m² resulting from ten successive CNF layers on the base sheet. The bar coating of CNF on the paper board was found not to substantially enhance its barrier properties, however did increase stiffness while reducing compressing strength [30, 31]. The cellulose nanofiber with multilayered resin coated on the paper board is proved to decrease the water vapour permeability of paper board. The coating is performed by the dispersion coating process or lithographic printing. [35]

Micro-fibrillated cellulose (CNF) and shellac were coated on the paper and paper board using a bar coater or a spray coating technique to enhance its barrier properties of the substrates. The coating performance is evaluated by the decreasing barrier properties of the sheet through decrease of the air permeance of the paperboard and papers with a multilayer coating of CNF and shellac. Furthermore, the oxygen transmission rate decreased several logarithmic units and the water vapour transmission rate reached values considered as high barrier in food packaging (6.5 g/m²/day). [36]

Although above mentioned conventional processes offers some advantages, they pose serious limitations such these methods should as they are done in batches and/or are not capable of producing high coat weight on the base sheet to achieve barrier properties of the sheet. Therefore, spraying is a potentially promising approach for the preparation of cellulose nanofiber sheet and coating of nano cellulose on the base sheet [29, 38].

Table 3.1: Coating Process of CNF

Type of Cellulose	Substrate	Methods	Function	Coat Weight	WVTR (g/m ² day)	OTR or Air Permeability	Reference
Cellulose Nano fibrils (CNF)	Packaging Paper board (178±4 gsm) and 190±5 µm.	Roll to Roll coating with slot	Packaging	10 g/m ² (0 -16 gsm)	500 -100	NA	[38]
Carboxy-methylated micro-fibrillated cellulose film	Kraft paper Grease proof paper Free standing film	Dispersion Casting	Packaging material	1.3 1.0 g/m ²	NA	0.3 nm/Pa s. 0.2 nm/Pa s 0.009 and 0.0006 cm ³ µm/ (m ² day kPa)	[22]
Micro-fibrillated cellulose	calendared paper (41 gsm)	Bar Coating Size Pressing	-	7 gsm 4 gsm	NA	786 ± 166 nm/Pa.s 4856 ± 1717 nm/Pa.s.	[31]
Micro-fibrillated Cellulose	Card board (300)	Bar Coating	-	17±1 gsm	NA	0.18±0.01 cm ³ /m ² pa.s	[30]
Cellulose nanofiber	Fibre based substrates	Foam Coating	Tailoring the surface properties of the sheet and Functionalization	0.3 -2 gsm	NA	NA	[29]
Micro-fibrillated cellulose	Composite paper	Forming and Dewatering-Filtration	CNF composite Paper	NA	NA	NA	[37]
Nano-emulsified Cellulose nanofibre	Addition of the Nano emulsified Cellulose nanofibre	Vacuum Filtration	Cellulose nanofibre sheet	NA	NA	2.75*10 ⁻⁰⁸ ± 0.9*10 ⁻⁸ K(m ²)	[39]

Type of Cellulose	Substrate	Methods	Function	Coat Weight	WVTR (g/m ² day)	OTR or Air Permeability	Reference
Micro-fibrillated cellulose	Porous Paper substrate	Spray Coating	Barrier and Mechanical Properties Enhancement	6 gsm	NA	Drastically Reduced	[6]
Graphite Carbon Black Micro – Fibrillated cellulose	Wet Paper Substrate	Spray Coating	Electrode	NA	NA	NA	[7]

3.2.4 Spray Coating of Nano Cellulose:

Spraying of cellulose nanofiber is an alternative technique for making nano-fibre sheets that has been used to produce either continuous self-standing films by spraying on to a fabric or to produce composite laminates by spraying onto a base sheet [6, 7]. Spraying has some significant advantages such as contour coating and contactless coating with the base substrate. The comparison of spray coating with other coating techniques is shown in Figure 3.2. The topography of the surface of the base substrate does not influence on the coating process.

- Contactless
- Contour coating
- Coating of tear sensitive material
- Controlling the coating material

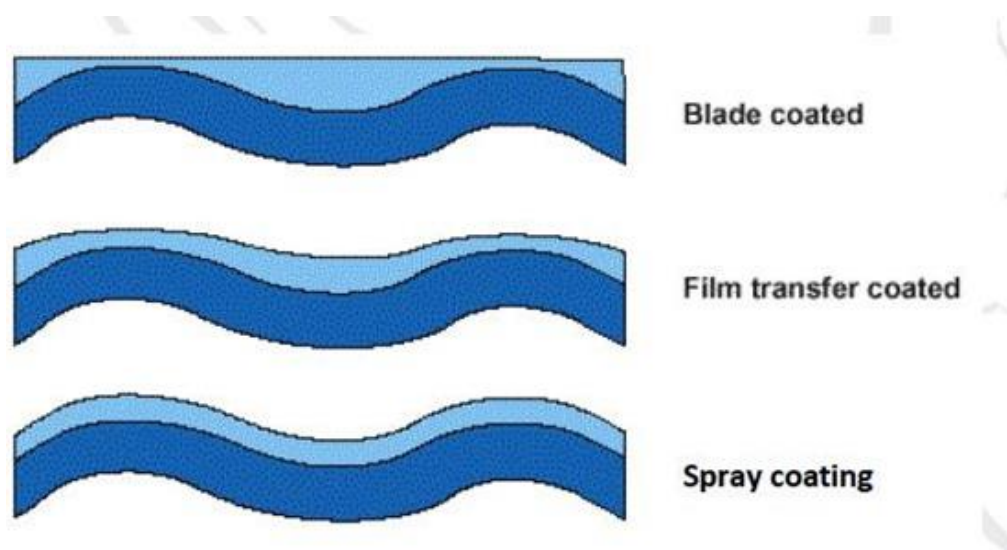


Figure 3.2: Concept of Spray coating and surface finishing. (Vilho Nisssonen, 2002) [48].

It is a novel technique for creating barrier film on the base surface rapid manner. Beneventi *et. al.* reported that the laboratory scale spray coating of micro fibrillated cellulose on different kinds of paper substrate enhances the barrier and mechanical properties of the spray coated sheet [6]. However, after spraying, they used vacuum filtration which is similar to the conventional paper making process to remove the excess water. As a consequence, it leads to time consuming process.

- a. **Spray Coating of Cellulose Nanofiber to Make Self Stand Cellulose Nanofiber Sheet:** Stand-alone Micro-fibrillated sheet have been prepared using either vacuum filtration or casting. Casting is a time consuming process as it typically requires three days for the film to dry and it is difficult to control the wrinkling of the film as it dries [40]. Vacuum filtration can be considerably quicker. It recently reported that the laboratory sheet preparation time for light weight sheets less than 60 g/m^2 has been reduced from three or four hours [41] to 10 minutes [42,43] by increasing the solids content above the gel-point, increasing the size of the filter openings to reduce filter resistance and using polyelectrolytes to control. However, there can be significant issues in separating the sheet from the filter and subsequent handling before it finally dried. In addition, in vacuum filtration method, the range of sheet basis weight that can be manufactured is limited, as the filtration time increases exponentially with sheet basis weight. In the case of spray coating, the range of basis weight achievable with spraying is much higher than has been obtainable with filtration. A maximum mass of the film of 124 g/m^2 was obtained by spraying micro-fibrillated cellulose onto a nylon fabric running at a speed of 0.5 m/min [5]. Spraying can also be performed at a higher initial solid content compared to filtration, reducing the amount of water that has to be removed in subsequent drying. Spraying has not so far been used to make discrete sheets for laboratory investigations, or for small scale products. It is still an open question about the sheet quality produced by spraying compared to hand sheets made by laboratory vacuum filtration. In this method, they failed to explain about the quality of cellulose nanofiber sheet through the uniformity of the sheet, surface roughness and smoothness, thickness and coat weight when high suspension concentration used and tailoring the barrier and mechanical properties of the cellulose nanofiber sheet prepared via different suspension of cellulose nanofiber.

3.2.5 Research Gap:

The literature reveals that spraying of cellulose nanofiber has been shown as a potential method to produced cellulose nanofiber layers on the base sheet to tailor its barrier and mechanical properties and to produce various cellulose nanofiber functional sheets and to replace sheet forming method. The following research gaps are observed and will be investigated through this research:

- The uniformity and surface topography of the spray coated cellulose nanofiber sheet in comparisons with sheet prepared via vacuum filtration is not understood.
- Similarly, the barrier and mechanical properties of spray coated cellulose nanofiber sheet in comparisons with the cellulose nanofiber sheet prepared via vacuum filtration is not understood.
- What range of materials can be produced and how can the process be controlled to produce sheets to the required properties. How does spraying of different suspension concentration of cellulose nanofiber affect the properties of the sheet?
- What is the effect of forming the cellulose nanofiber-inorganic composites by spraying to improve barrier properties and mechanical properties of the nano-composite?
- The spray coated process could be adapted to make continuous or standalone sheets to replace the conventional vacuum filtration process.

3.3 Rapid Preparation of Cellulose Nanofiber Film by Spray Coating Method:

3.3.1 Introduction:

This research describes a novel, highly efficient method for the laboratory production of cellulose nano- fibre sheets by spraying cellulose nanofibre directly either on to circular steel plates or various fibre base substrates to produce barrier materials. The cellulose nano-fibre sheets formed in this way then can be subsequently dried in air under restraint without having to separate the sheet, maximising the rate at which the sheets can be produced. In this work, we also compare the quality of the sheets formed, as measured by the variation in thickness, and compare it to sheets formed by filtration. Micro-fibrillated cellulose (CNF) supplied from DAICEL Chemical Industries Limited (Celish KY- 100S) was used to prepare films. CNF sample was used at consistencies ranging from 0.5 to 2.0 wt. %, prepared by diluting the original concentration of 25 wt. % with distilled water and mixing for 15,000 revolutions in a disintegrator. The viscosity of the CNF suspension was evaluated by the flow cup method which evaluates the process of coating fluid flow through an orifice to be used as a relative measurement of kinematic viscosity expressed in seconds of flow time in DIN-Sec.

3.3.2 Preparation of Micro-Fibrillated Films Through Spray Coating and Vacuum Filtration Methods:

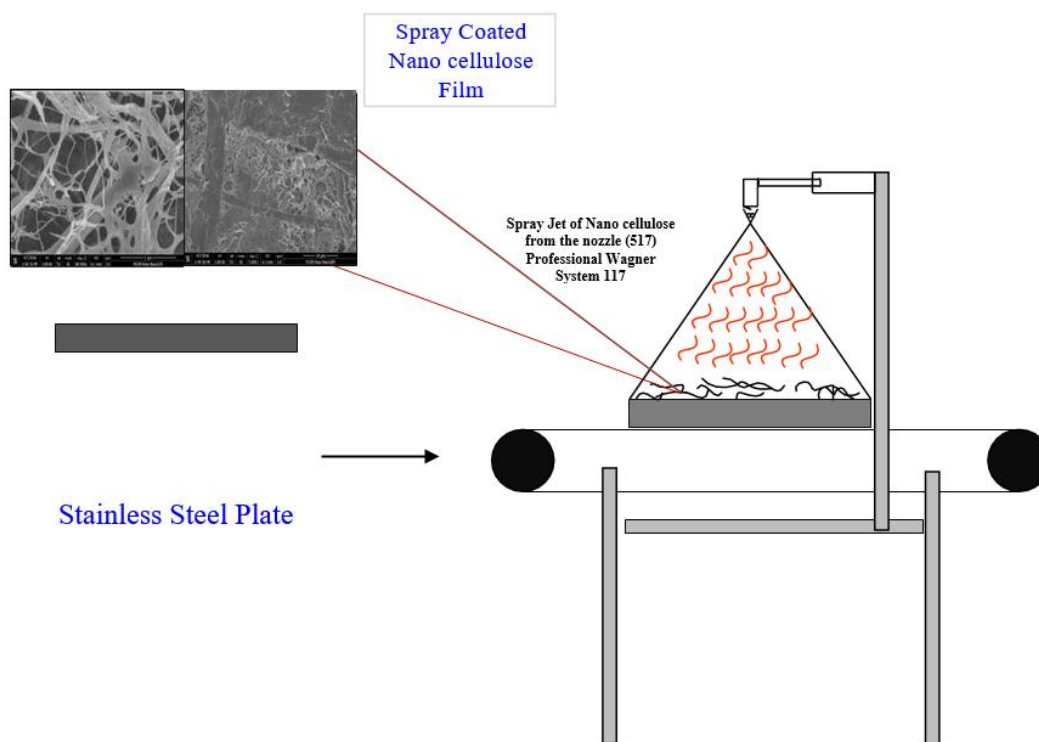


Figure 3.3: Experimental Set up for Lab Scale Spray Coating System for Preparation of Nano cellulose Film.

After spraying, the film on the plate was dried under restraint at the edges for at least 24 hours. The CNF film can then be readily peeled from the stainless steel plate and stored at 230C and 50% RH for further testing. For comparison, nanofiber films were also prepared using vacuum filtration method as reported in [10]. In brief, CNF suspension with 0.2 wt. % concentration was poured into a cylindrical container having a 125 mesh filter at the bottom and then filtered until it formed a wet film on the mesh. The wet film was carefully separated using blotting papers and then dried at 1050C in drum drier for around 10 minutes. The film prepared by this method is used as a reference film to compare the uniformity and thickness of the spray coated film. The basis weight (g/m^2) of each micro fibrillated cellulose sheet was calculated by dividing the weight of the sheet, after 4 hours drying in the oven at a temperature of 105 °C, by the sheet area.

3.3.3 Evaluation of Thickness Distribution and Thickness Mapping:

The Micro fibrillated sheet thickness was measured utilizing L&W thickness analyzer (model no 222). The circular CNF sheets were divided into six regions and measure thickness in six locations of each region. The thickness mapping of centre rectangular region of the circular sheet are done by plotting contour plot using Origin Pro 9.1. The visual explanation is given in the figure 4. The thickness of the sheets in six locations of each region is measured and averaged. A x cm square section in the middle of each sheet was tested for thickness variation by measuring a matrix of 6 X 6 evenly spaced points for thickness mapping. The information on thickness mapping is added as supplementary information. The mean thickness of all the sheets is plotted against the suspension concentration of Nano-cellulose. The mass of the film per unit area is evaluated for various concentration of Nano cellulose sprayed on the stainless steel plate.

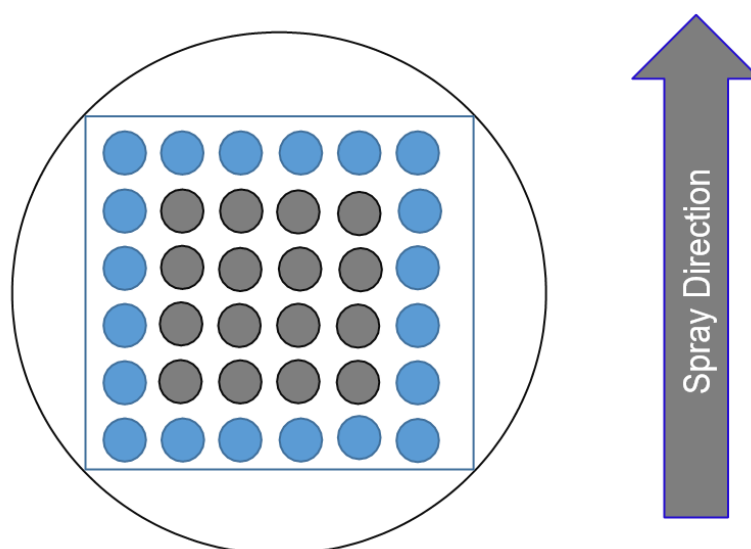


Figure 3.4: Mapping of thickness of the micro-fibrillated sheet. The thickness is measured in the centre region of the sheet. The square section of centre part of the sheet is used for contour plotting. The grey point of thickness used for mapping to confirm the uniformity of the sheet.

3.3.4 Surface Topography of Nano fibrillated Sheets:

The surface morphology and topography of the iridium coated nano-sheet prepared at a conveyor speed of 0.32 cm/sec are performed with FEI Novo SEM. The images of both surface of the nano sheets are captured at magnification from 1 μm to 100 μm in secondary electron mode-II of FEI Novo SEM. Furthermore, the surface roughness of both sides of the film at nanoscale is evaluated by atomic force microscopy.

3.3.5 Result and Discussion:

a. Effect of Suspension Concentration on Viscosity of Cellulose Nanofiber:

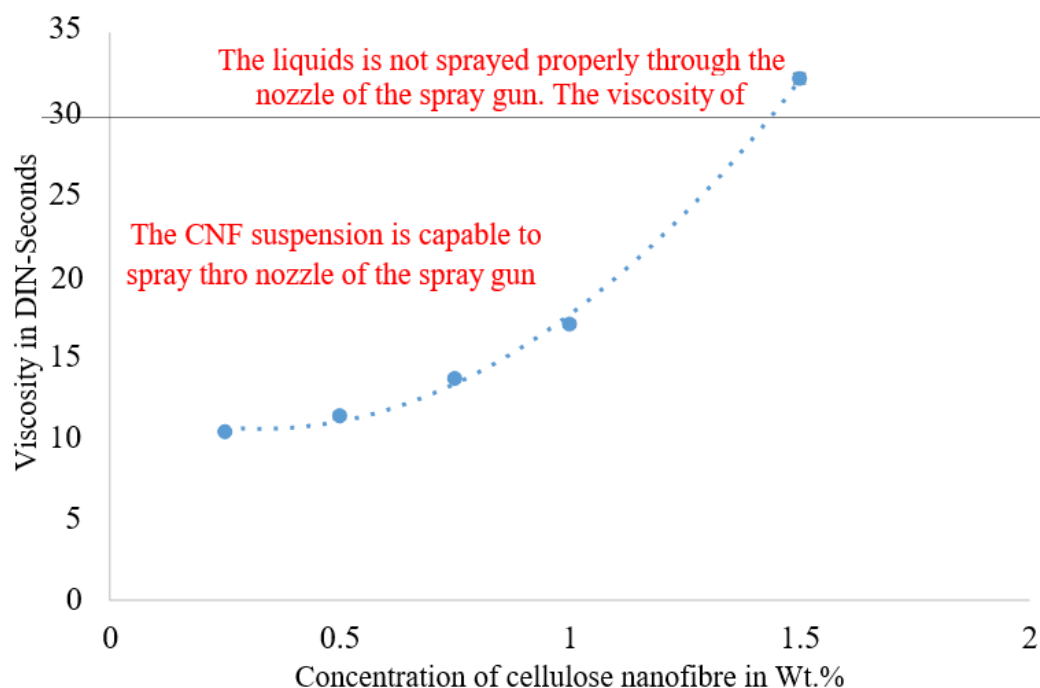


Figure 3.5: Viscosity of cellulose nanofiber suspension using dip cup method

Effect of suspension concentration on the viscosity of cellulose nanofiber is given in figure 5. It increased with solid/ fibre content in the suspension. The efflux time < 30 sec confirms the sprayable concentration of cellulose nanofiber for coating operation. The viscosity of 1.5 wt. % CNF suspension is 32.18 ± 0.94 DIN Sec predicted by dip cup method. It is quite challenging to predict the efflux time and viscosity of cellulose nanofiber suspension beyond the concentration of 1.5.Wt. %. It is reported that cellulose nanofiber suspension could form a gel like structure and behave shear thinning rheology even at low concentration of CNF in the suspension. The viscosity of cellulose nanofiber suspension increase with increasing concentration of fibres content in the suspension [44]. The rheological properties of CNF suspension are influenced by fibre morphology, orientation and aggregation. It is also reported that the viscosity of suspension increases with fibre aspect ratio and becomes

substantially higher for high suspension concentration [45] When the CNF suspension concentration is higher than 2.00 wt. %, CNF suspension has lost its fluidity, becomes like stiff gel and also viscosity is higher than 32.18 DIN Sec after dispersion in water after disintegration of fibres. Onwards of this concentration above 2 wt. %, CNF suspension behaves as a viscoelastic fluid and formation of network of entangled cellulose fibrils which causes gel-like behaviour [46] [47]. The spraying such high solid content suspension is really challenging because more chance of clogging the nozzle. Furthermore, the high shear force is required to pump and spray the high fibre content of the slurry.

b. Effect of Suspension Concentration of Thickness and Basis weight of the NFC film:

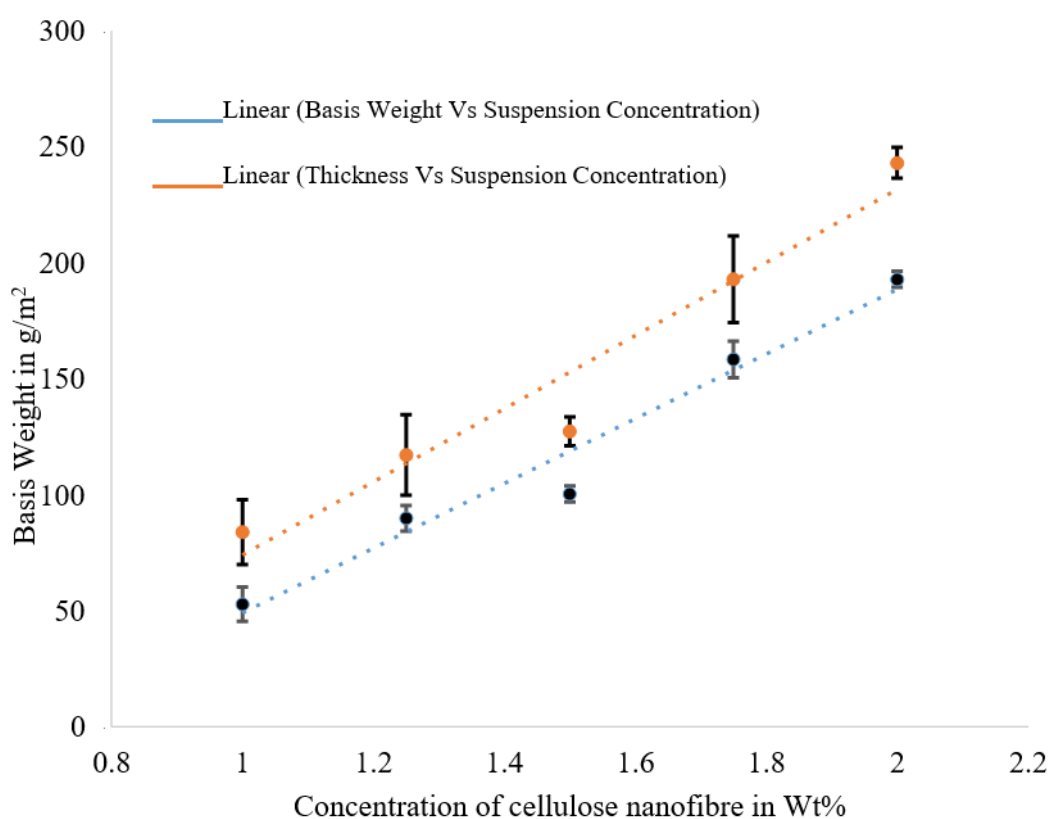


Figure 3.6: Effect of suspension concentration on the basis weight of the nano cellulose film prepared using spray coating technique at a constant velocity of 0.32 cm/sec.

The stable and homogeneous films were prepared with various concentrations of CNF suspension via spray coating technique as described in the experimental section. The operational range for spraying cellulose nanofiber suspension was between 1.0 wt. % and 2.0 wt. %. Below 1 wt. %, the suspension was too dilute and flowed over the metal surface producing an uneven film difficult to peel from the plate after drying. Above 2% wt., the suspension become too viscous to spray. The lower and upper limits, corresponded to suspension viscosities of 17.0 ± 0.6 to 32.2 ± 0.9 DIN sec, respectively. Figure 6 shows the effect of cellulose nanofiber suspension concentration on the basis weight of the film and

mean thickness of the film. Each point is the average of 4 replicates with the error bars providing the standard deviation. Both sheet basis weight and thickness increased approximately linearly with increasing cellulose nanofiber suspension concentration. Basis weight range from 52.8 ± 7.4 to 193.1 ± 3.4 g/m² by spraying suspension with concentration of 1.0 and 2.0 wt. %, respectively; film thickness was 83.9 ± 13.9 μm and 243.2 ± 6.6 μm for the lowest and highest consistencies.

Figure 3.7 presents the contour plot of the thickness distribution of the 1.5 Wt. % spray coated film compared with a film made by the established method of vacuum filtration. The basis weight of the sheet prepared by spray coating and vacuum filtration are almost identical at 100.5 ± 3.4 g/m² and 95.2 ± 5.2 g/m², respectively. The spray direction was from bottom to top. The full set of data obtained at all basis weights is given in the supplementary material. Compared to spray coating, vacuum filtration required a much higher dewatering time of 15 minutes to produce the sheet.

When compared to the sheet made from vacuum filtration, the spray coated micro – fibrillated cellulose sheet is slightly thicker, even when correcting for the slight difference in basis weight. The apparent density of the spray coated sheet and sheet prepared via vacuum filtration were 793 and 834 kg/m³, respectively. In addition, there is a somewhat wider distribution of thickness for the spray- coated film. The thickness of the CNF film sheet prepared via vacuum filtration process and spray drying were 113.4 (5.4) μm and 127.1 (12.1) μm, respectively. The numbers in brackets give the standard deviation of the distribution of measured thickness. The measured standard deviations of thickness for each sheet were normalized by the average thickness. For the thinnest, lowest basis weight sheets made at 1.0 wt. % consistency, the normalized value was 52.8 ± 7.4 g/m², in comparison to a value of 193.0 ± 3.4 g/m² for the sheets made at 2.0 wt. % consistency. The significant reduction in variability is most likely due to the more rigid suspension at 2.0 wt. % consistency, which produces a more stable suspension sprayed onto the surface of the plate.

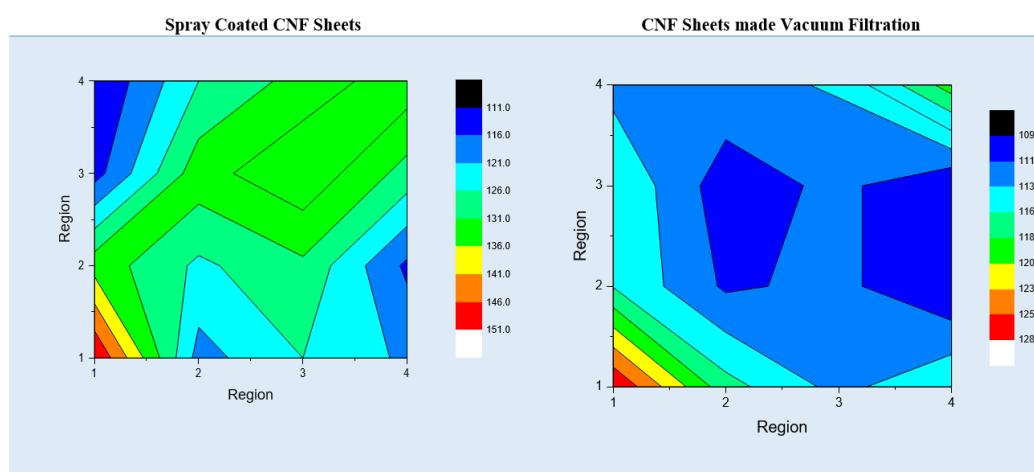


Figure 3.7: Thickness Distribution of the cellulose nanofiber sheets –Spray coated at Conveyor velocity of 0.32cm/sec and Vacuum Filtration

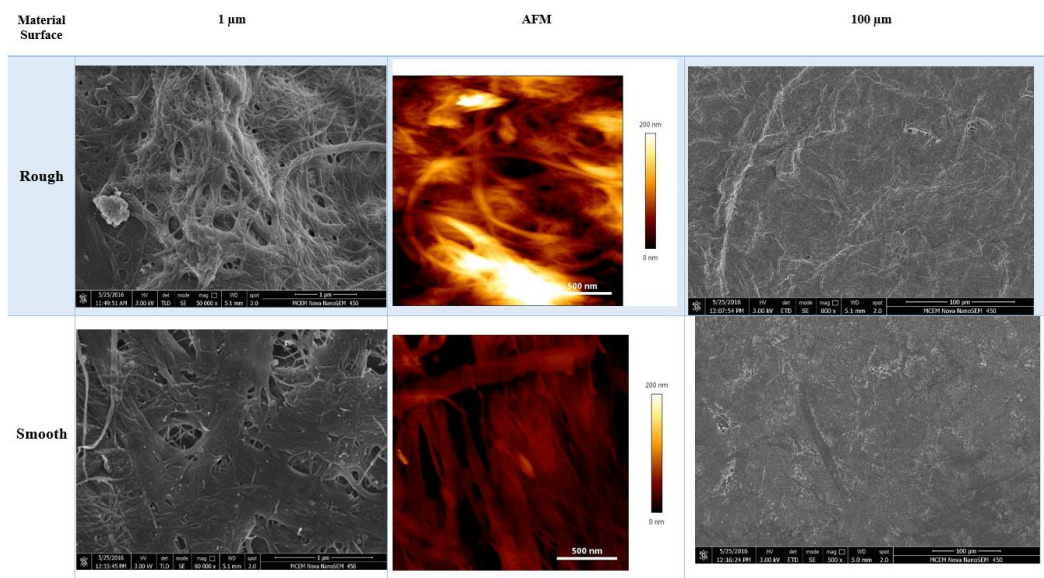


Figure 3.8: SEM image of the cellulose nanofiber sheet – Rough and Smooth surface and AFM Image of the both sides of the CNF Film.

Figure 3.8 shows the surface morphology and topography of both sides of the spray coated micro- fibrillated cellulose sheet investigated by scanning electron microscopy and atomic force microscopy (AFM). At all the length scales investigated, the surface in contact with the stainless steel plate is notably smoother and less porous than the reverse side, where some fiber clumps from the suspension were retained in the sheet surface as it dried. Visually the smooth surface of the sprayed film has a glossy, shiny appearance. Roughness was quantified from the AFM images. The RMS roughness of the rough side is 414.0 nm for 10 μ m x 10 μ m film area and 51.4 nm for 2 μ m x 2 μ m film area whereas the surface roughness of the glossy side in root mean square (RMS) is only 81.1 nm for 10 μ m x 10 μ m film area and 16.7 nm for 2 μ m x 2 μ m film area. AFM measurements of the sheet prepared by filtration are given in the Supplementary information and show both sides had a surface roughness of 417.7nm (Side 1) and 330.8 nm (Side 2) at an inspection area of 10 μ m x 10 μ m, which is approximately the same as the rough side of the sheet prepared by spray coating. The results reported in this investigation confirm that a laboratory scale spraying of various concentration of micro-fibrillated cellulose on a stainless steel plate is viable for the rapid preparation of micro-fibrillated cellulose sheet with basis weight ranging from 52.8 \pm 7.4 to 193.1 \pm 3.4 g/m². The basis weight of the sheet was readily controlled by the concentration of micro-fibrillated suspension sprayed on the stainless steel plate at a constant velocity of conveyor. In our investigation on spraying, the processing time was 50.2 seconds to spray 15.9 cm diameter sheets, independent of the basis weight from 52.2 to 193.1 g/m². The quickest time reported in the literature for sheet formation with filtration was from work in our group (Varanasi and Batchelor 2013), where 2.8 minutes was required for filtering a low basis weight of 56.4 g/m², formed from 0.6 wt. % suspension. In contrast the 95.1 g/m² sheet formed at 0.2 wt. % made for the work in this paper took 15 minutes to filter, with filtration time exponentially increasing with sample basis weight. After filtering, the micro-fibrillated sheets can often be difficult to separate from the filter, taking additional time to complete the transfer to the blotting paper without destroying the sheet. Drying the filtered

sheet then requires repeatedly manually feeding the sheet into a rotating drum dryer until dry, with the overall process taking at least 10 minutes from the start of filtration. In the spray coating method, the drying time for Nano cellulose sheets in ambient conditions is from 24 hrs to 48 hrs, which is reduced to 30-60 minutes when drying in an oven at 105°C. However, while the total time to prepare and dry a sheet is longer with spray coating a stainless steel plate, the key strength of the method is the reduction in operator time. Leaving aside, the preparation of the cellulose nanofiber suspension, which is common for the two methods, preparing 10x100 gsm sheets requires less than 9 minutes of operator time with spraying compared to 220 total minutes with filtration.

Mechanical and Barrier Properties of Spray Coated Cellulose Nanofiber Sheet:

Optimization of Velocity of the Conveyor:

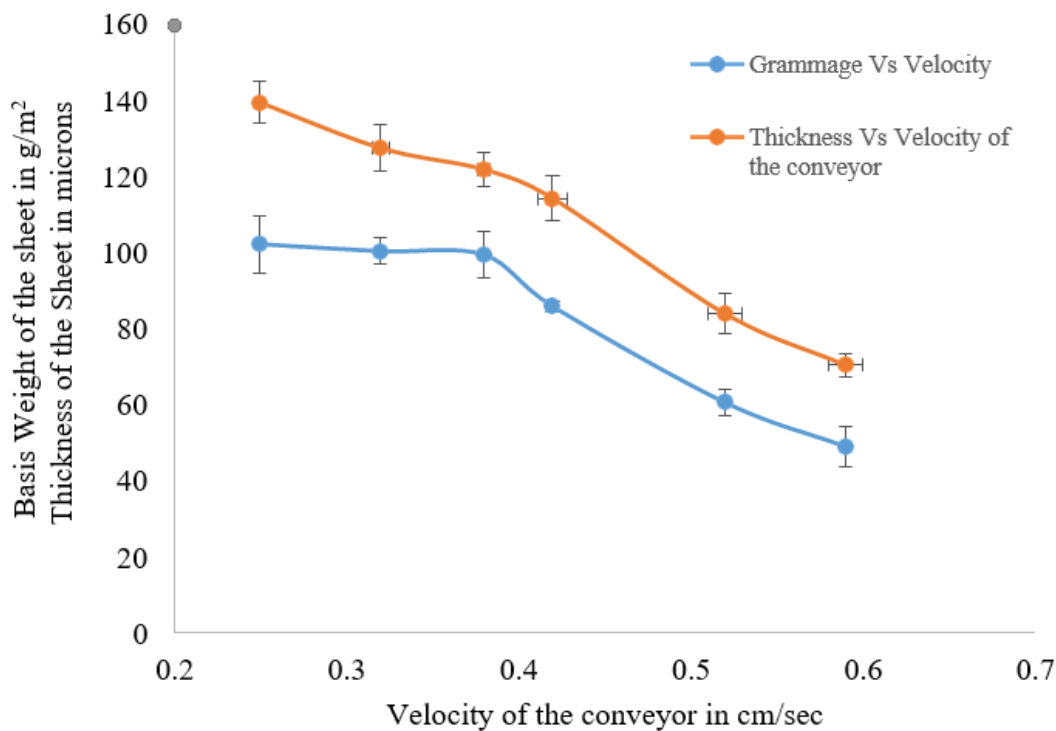


Figure 3.9: Effect of the velocity on the basis weight of the CNF sheet and Figure 3– Effect of Velocity of the conveyor on thickness of the spray coated sheet

The Figure 3.9 explains about the effect of the velocity of the conveyor on the basis weight of the cellulose nanofibre sheet prepared by spray coating process and how it does influence on the spraying time of cellulose nanofibre on the stainless steel plated indirectly and as a consequence, the basis weight of the sheet is varied from 45 to 100 g/m². The figure confirms that the basis weight of the cellulose nanofibre sheet is controlled by the velocity of the conveyor.

Formation Test for Spray coated sheet at Different Velocity of the Conveyor:

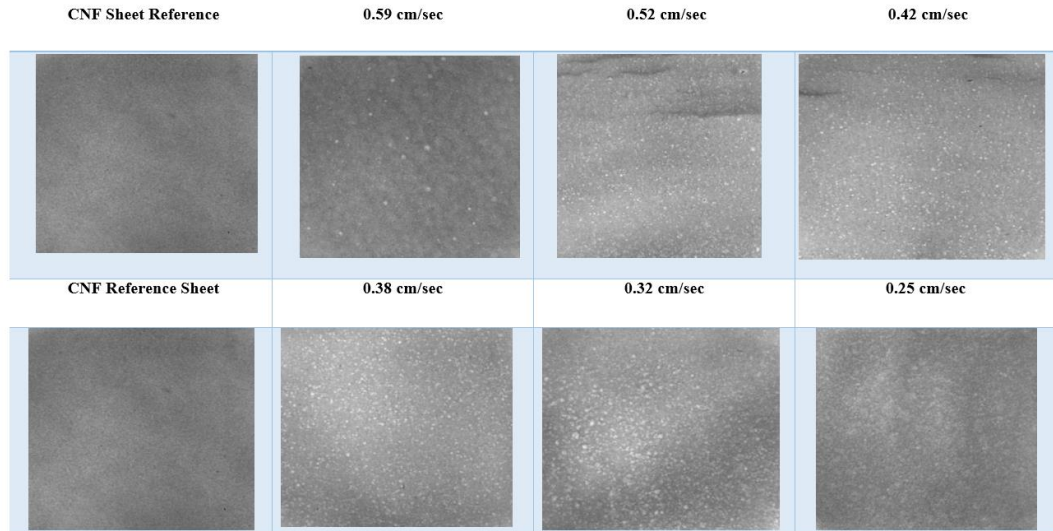


Figure 3.10: Uniformity of the spray coated sheets prepared at various velocity of the conveyor

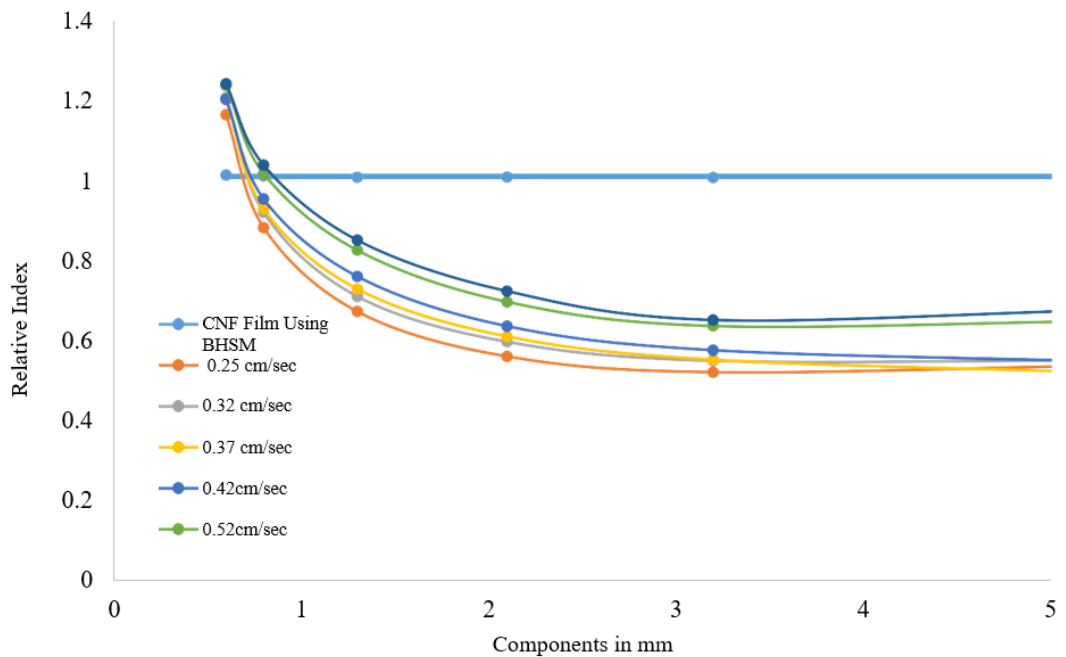


Figure 3.11: Formation test of Spray Coated sheet prepared at various of velocity of the conveyor

Figure 3.10 and 3.11 shows the effect of velocity on the uniformity of free standing CNF film. These figures conclude that the uniformity of the film can be increased at lowest velocity. At lowest velocity, more CNF suspension deposited on the base surface forms thick and uniform films.

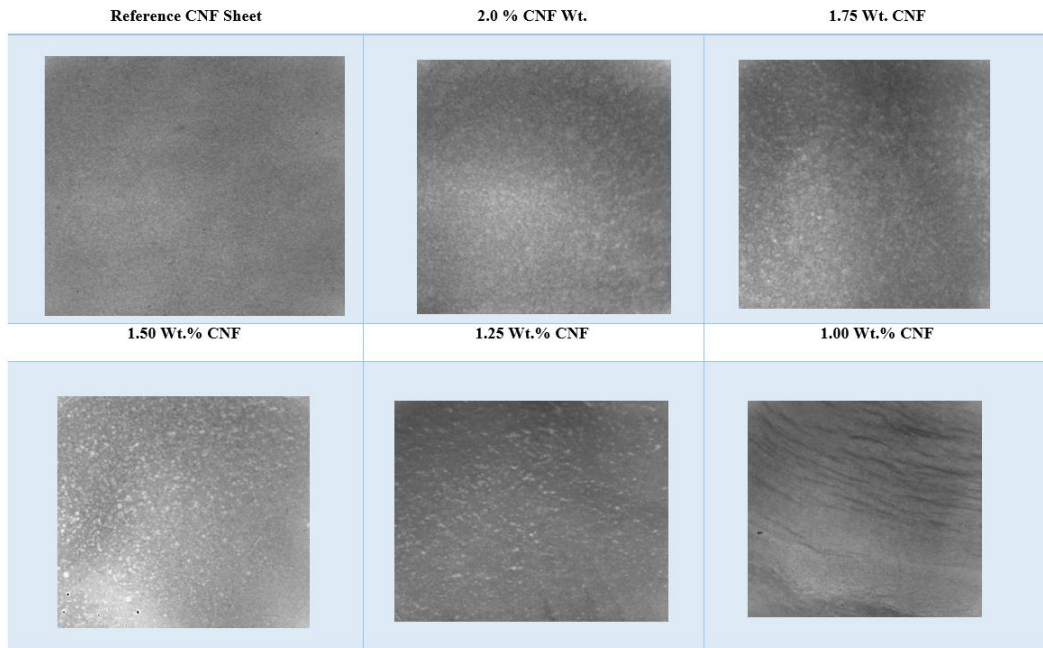


Figure 3.12: Uniformity test of spray coated paper prepared different suspension of CNF

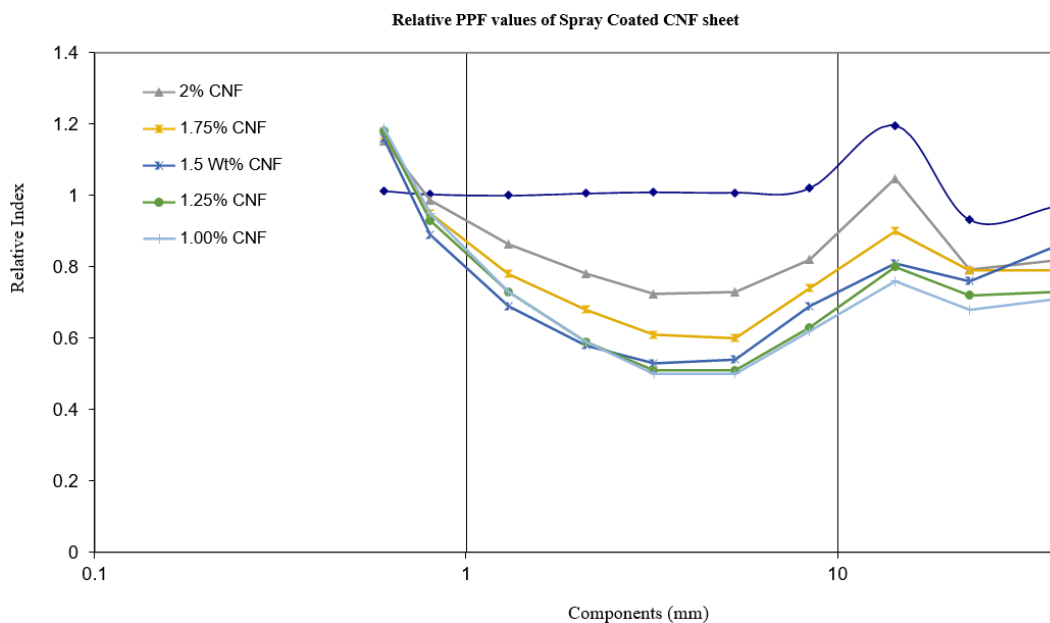


Figure 3.13: Formation Test of Spray Coated sheet made by different suspension of CNF

Figure 3.12 and 3.13 the effect of CNF suspension consistency on the uniformity of the film. The CNF suspension consistency increase the uniformity of the film also increased.

Effect of Suspension Concentration on Apparent Density of the Sheets:

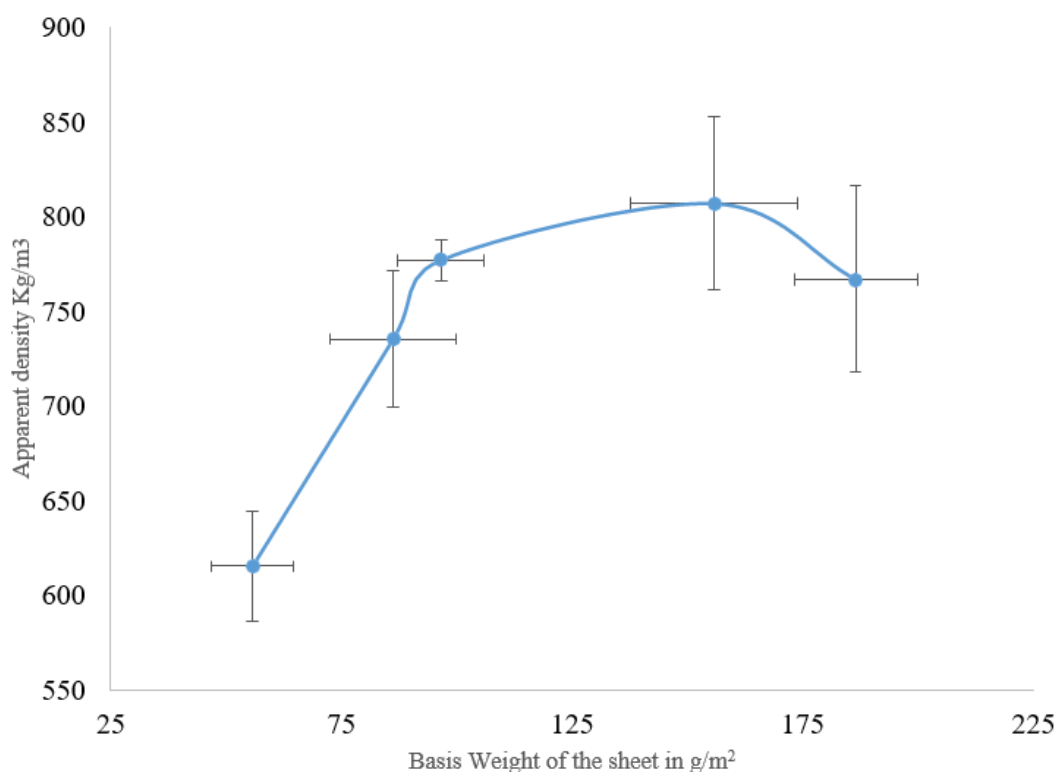


Figure 3.14: Effect of suspension concentration on apparent density of cellulose nanofibre sheet.

The Figure 3.14 explains the effect of suspension concentration of cellulose nanofibre sprayed at constant velocity of the conveyor on the stainless steel plate on the apparent density of the cellulose nanofibre sheet. The apparent density of the cellulose nanofibre sheet increased with the suspension concentration sprayed on the stainless steel. The apparent density of the sheet increased through increasing thickness of the sheet and basis weight of the sheet. The figure investigates the effect of the basis weight of the cellulose nanofibre sheet prepared via spraying on the stainless steel plate on the apparent density of the sheet. The apparent density of the sheet linearly with basis weight of the sheet up to 96.6g/m² and then it is almost constant in apparent density of the sheet.

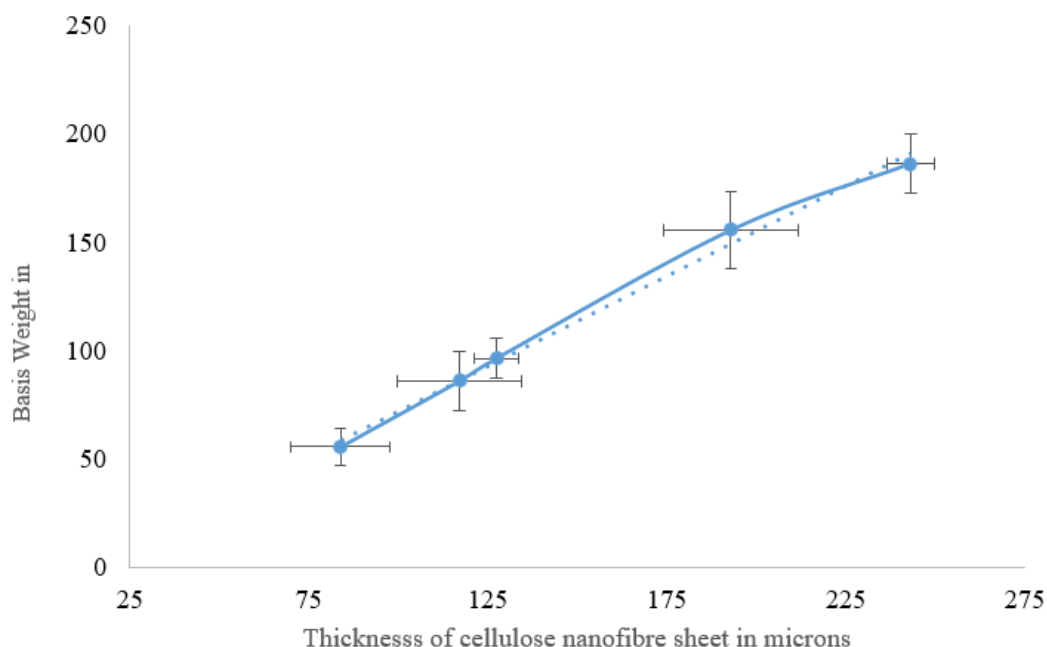


Figure 3.15: Effect of thickness of the cellulose nanofibre sheet on the basis weight

The Figure 3.15 investigates the effect of thickness of the nano cellulose sheet prepared by suspension concentration from 1.0 wt.% to 2.0 wt.% sprayed on the stainless steel plate and evaluated its basis weight of the sheet. The plot between thickness of the cellulose sheet and basis weight of the sheet is a linear relationship.

Barrier Properties of the Cellulose Nanofiber Sheet:

The barrier properties of the cellulose nanofiber sheet are evaluated by measuring the air permeability of the sheet and water vapour transmission rate of the cellulose nanofiber sheet.

Air Permeability of the CNF Sheets:

The air permeability of the cellulose nanofiber sheets prepared via spraying at various velocity of the conveyor and different concentration of CNF suspension are impermeable. The effect of velocity of the conveyor does not influence on the barrier properties of the sheet. The air permeability of the cellulose nanofiber sheet is $< 0.003 \mu\text{m}/\text{Pa.S}$.

Mechanical Properties of the Spray Coated Sheet:

Influence of Suspension concentration on Mechanical properties of spray coated CNF Sheet:

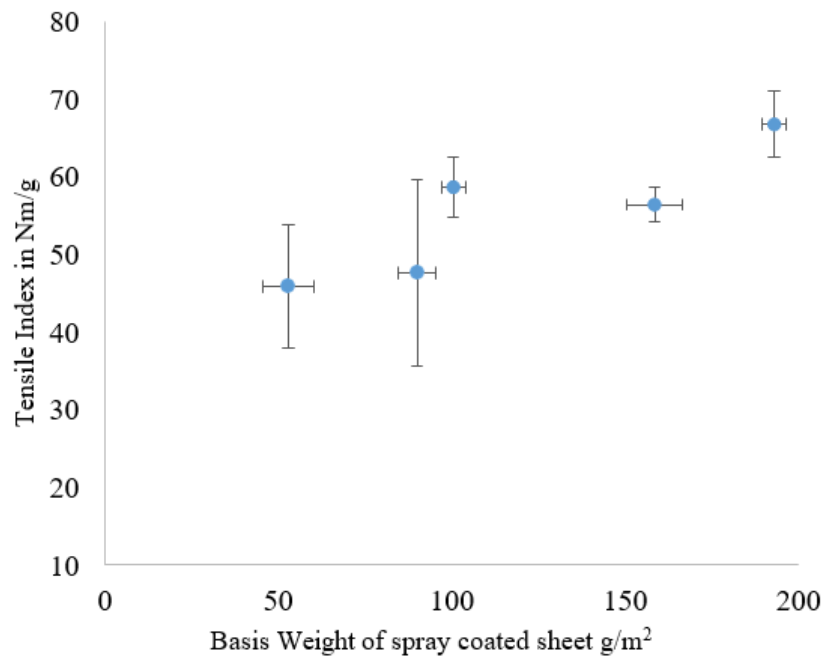


Figure 3.16: Tensile Index of the spray coated sheet.

The tensile index of the spray coated sheet increased with increasing its basis weight.

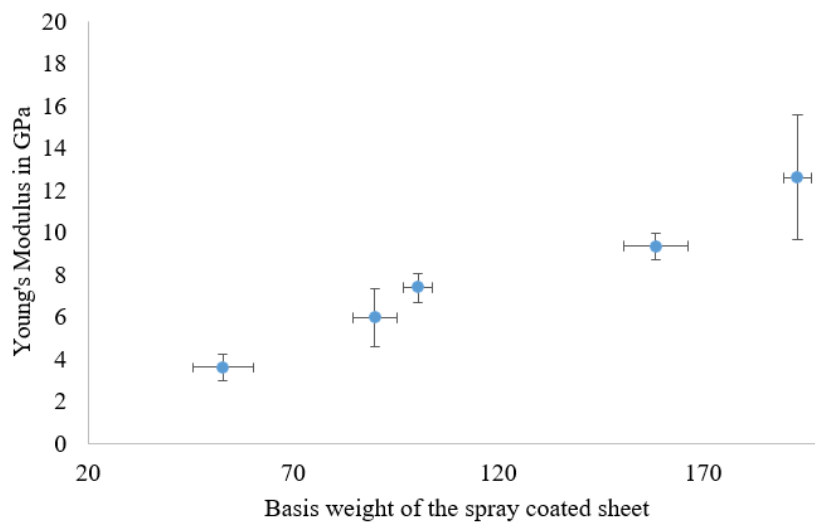


Figure 3.17: Young's modulus of the spray coated sheet

The young's modulus of the spray coated CNF sheet increase with the suspension concentration of cellulose nanofiber sprayed on the base surface.

Effect of The Velocity of the Conveyor on Tensile Properties of the Sheet:

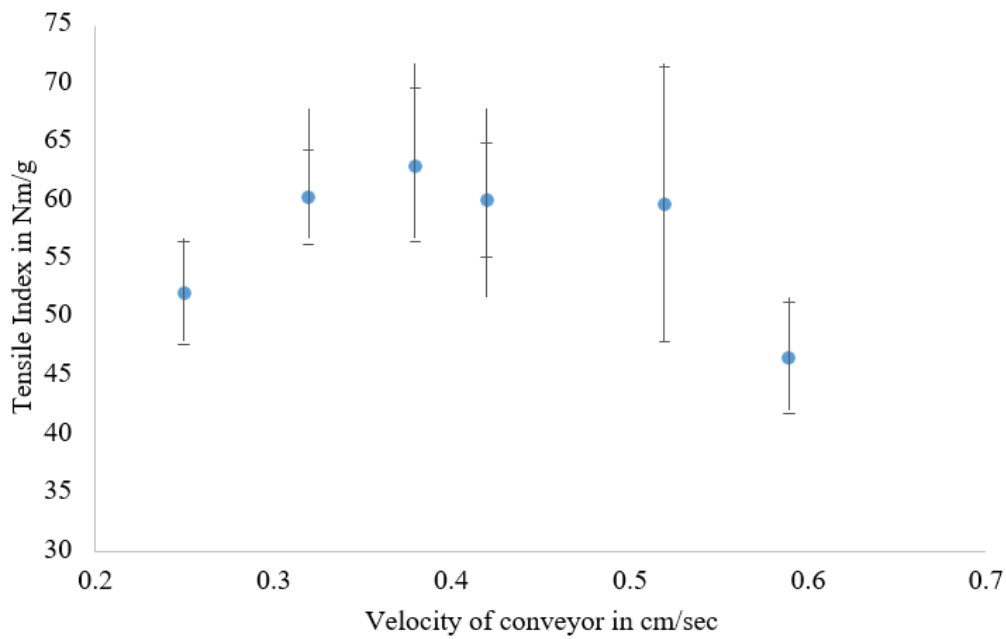


Figure 3.18: Influence of conveyor velocity on Tensile Index of the spray coated sheet. The tensile index of the spray coated sheet altered when the velocity of the conveyor is varied.

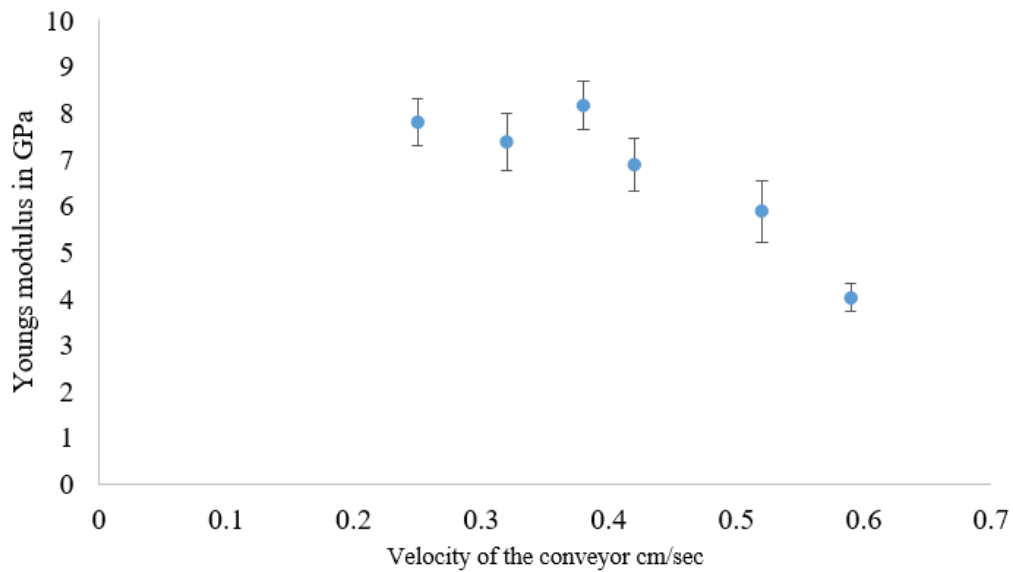


Figure 3.19: Influence of Conveyor Velocity on Young's Modulus of the spray coated sheet

The young's modulus of the spray coated CNF sheet increase with decrease velocity of the conveyor in the experimental set up.

Zero Span Test for Spray Coated Micro Fibrillated Sheet:

Influence of the Suspension concentration:



Figure 3.20: Zero span test of spray coated sheet prepared by different concentration of CNF. Influence of Velocity of the conveyor:

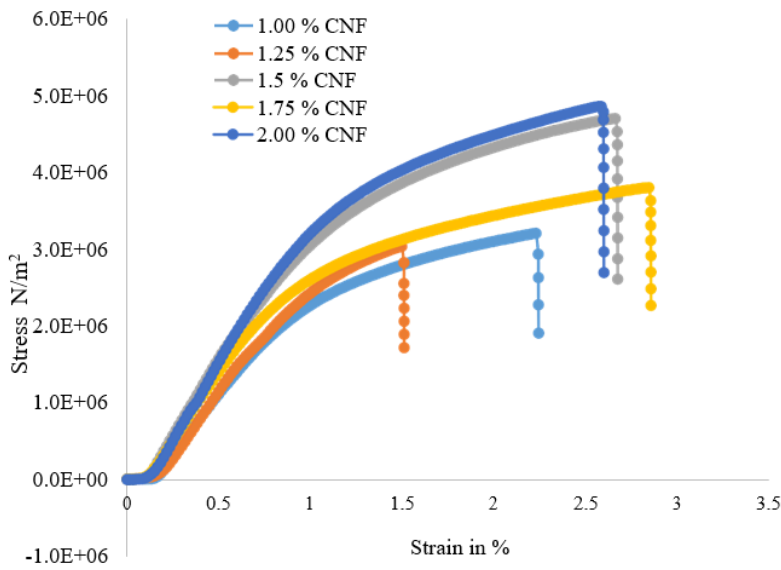


Figure 3.21: Influence of velocity of conveyor on the spray coated sheet.

The Figure 3.20 and 3.21 shows the zero span tensile indexes increased with the suspension consistency of CNF and decreasing the velocity of the conveyor.

Stress and Strain Curve for Spray Coated Cellulose Nanofiber Sheet:

Influence of suspension concentration:



Effect of Velocity of the Conveyor:

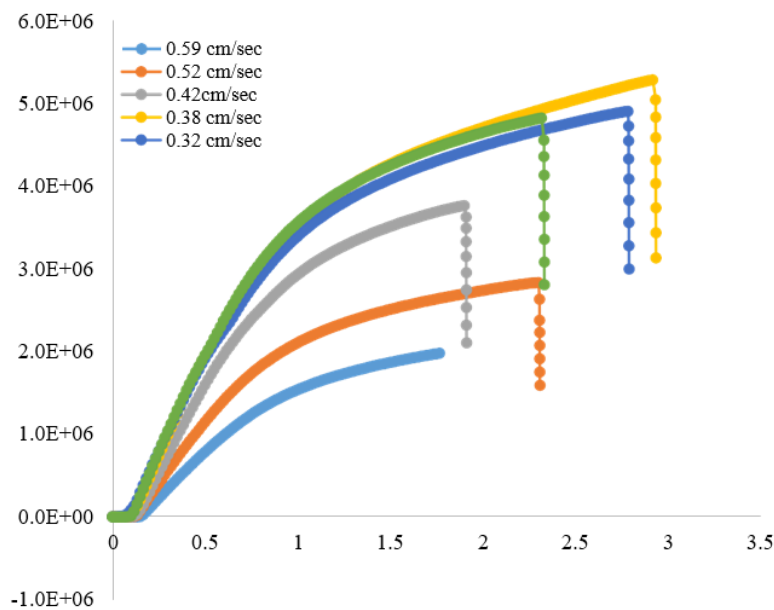


Figure 3.22 and 3.23: Stress and strain curve for CNF Film

Figure 3.22 and 3.23 shows the stress and strain curve for pure cellulose nanofibre film prepared via spraying. Figure 3.22 reveals that the strength of the film increased with increased CNF concentration. The sheet produced from lower CNF suspension concentration has flimsy in thickness and contains mark of ripples on the sheet. The sheet has very strong and good mechanical strength once the higher CNF suspension concentration sprayed on the steel plate.

The optimization of conveyor's velocity is another parameter for controlling CNF film properties. Figure 3.23 confirms the effect of conveyor's velocity on the stress – strain curve of the CNF films. At lower conveyor speed, the cellulose nanofibres are deposited large on the stainless steel plate. The film has well in strength when the film fabricated via spraying 1.5 wt. % CNF on the plate kept in a moving conveyor at a velocity of 0.32 cm/sec. At higher velocity, the CNF are less deposited on the steel plates and the sheet becomes very flimsy after drying and lowest strength.

Summary:

Spraying of micro-fibrillated cellulose suspension onto a polished stainless steel surface to make smooth films with a basis weight ranging from 50 to 200 g/m², simply by adjusting the suspension consistency, is an efficient technique at laboratory scale.

This method confirms the faster formation of the sheet within a minute on the solid surface. Further, Spray-coating on to stainless steel creates a two- sided film structure with a very smooth surface in contact with the stainless steel plate.

3.4 Spray Coating of Cellulose Nanofiber on the Base Sheet:

The spraying cellulose nanofibre on the base sheet (Brown paper -Packaging material) could boost their barrier properties. Initially, the spraying of cellulose nanofibre on the packaging paper using domestic spray gun is performed.

The spray coated brown paper is characterized for evaluation of performance of laboratory scale spray deposition method. Based on the laboratory scale performance of coating, the spray coating is upgraded with Professional spray gun integrated with Dow web coater for continuous process coating.

3.4.1 Materials and Methods:

Micro fibrillated cellulose (CNF) supplied from DAICEL Chemical Industries Limited (Celish KY-100S evaluation) was used for spraying operation for coating purpose. The domestic spray gun is used for spraying cellulose nanofibre on the base sheet.

The spray pattern is elliptical and the distance between spray nozzle and paper substrate is 20±2 cm. The coating of cellulose nanofibre on the paper substrate is one layer. The spray coated sheet is dried in the air drying under standard laboratory conditions.

3.4.2 Results and Discussion:

Effect of Suspension Consistency on Basis Weight:

The figure 9 shows the effect of suspension concentration on the coat weight. Using lab scale spray coating, the maximum of 25-35 g/m² on the base sheet is spray coated with concentration of 1.5 wt. % of Micro fibrillated cellulose. At this concentration of spray coating of CNF on the base sheet, it forms film over the surface and this film acts as barrier materials.

Effect of Basis Weight of the Coating on the Base Sheet on Air Permeability:

The figure 10 shows the effect of coating weight on the base sheet on air permeance. The basis weight of the coating on the base sheet increased with suspension concentration of cellulose nanofibre and after 1% cellulose nanofibre concentration, the barrier properties of the coated sheet is enhanced. Additionally, the air permeance of the spray coated sheet drastically reduced from 3.5 to < 0.003 $\mu\text{m}/\text{Pa. sec}$.

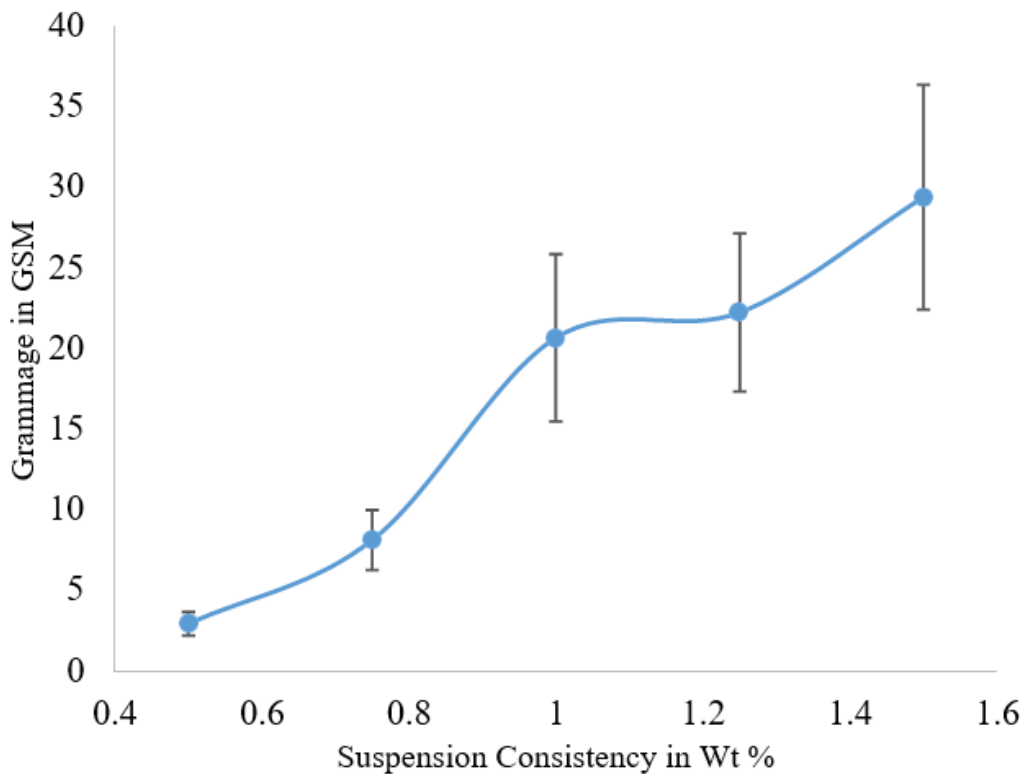


Figure 3.9: Plot of Coat Weight on The Base Sheet Against Suspension Consistency

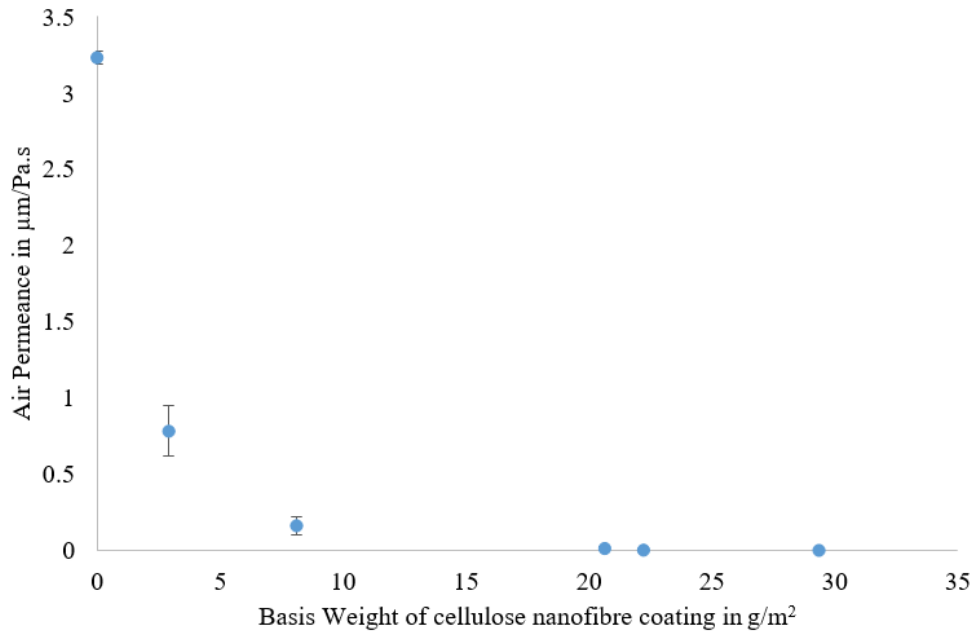


Figure 3.10: Plot Between Air Permeance vs Coat Weight

SEM Studies on Coated Surface:

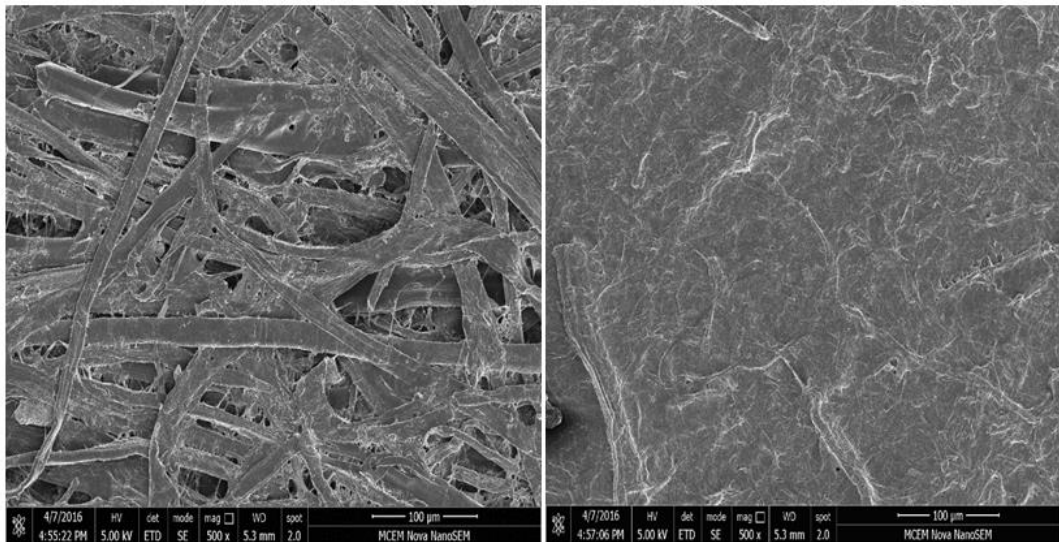


Figure 3.11: Micrograph of Coated and Uncoated Paper

The Figure 3.11 shows the micrograph of the spray-coated paper with 1.25 Wt. percentage of the micro-fibrillated cellulose at low magnification. The micrograph (100μm) shows the deposited cellulose fibres clumps and fibres on the surface of the base sheet. It also confirmed the different size of the fibre entangled with cellulose fibres clumps on the

surface. Moreover, the micrograph (100 μ m) confirms the complete coverage of micro-fibrillated cellulose coating formulation on the base sheet. When compared to the micrograph (100 μ m) of the uncoated paper, the coated paper showed that the coating formulation filled many surface pores and void space between the cellulose fibres.

3.5 Continuous Web-Spray System:

3.5.1 Scale Up from Laboratory Scale to Continuous Process:

The spray coating of micro-fibrillated cellulose on the stationary paper using domestic spray gun confirmed promising results. However, these experiments have to be carried out batch wise. The integrated Dow web coater with professional Wagner spray system is developed for preparing similar spray coated material in a continuous mode.

3.5.2 Experimental Setup and Trial Run:

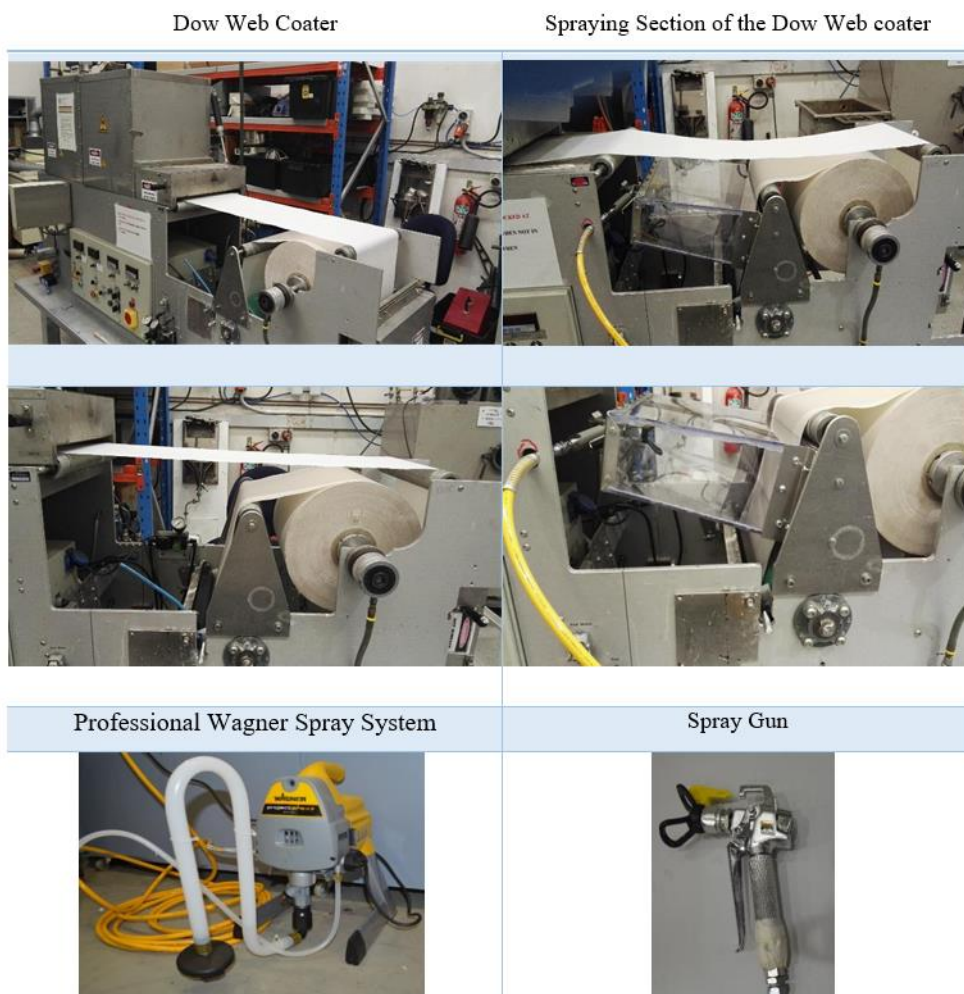


Figure 3.12: Components of Dow Web Coater Integrated with Spray System

3.5.3 Preliminary Results:

The suspension (CNF) sprayed on the base sheet is 1.5 Wt. % using this integrated Dow web coater with spray system. The CNF suspension from 0.5 to 1.00 Wt. % is also sprayed on the base sheet, due to continuous movement, the coating fluid is not stagnant on the base sheet and poor adsorption of the brown paper.

3.5.4 Limitations in The Experimental Set Up:

In the experimental setup for continuous process coating, the spray coated paper is stick to the other side of the paper when rewinding in the Dow web coater. It affects the coating surface on the base sheet. This problem arises due to the improper drying of the coated sheet in the dow web coater. Another limitation is dripping of the coating fluid from the base sheet due to moving from downward to upward in the Dow web coater.

The spray gun is planned to locate on top of web near to the infrared heater 1 in the Dow coater. This rearrangement might help to prevent the dripping of coating fluid on the base sheet and coating could be retained on the base sheet.

3.6 Conclusion:

The preliminary results reported in this section confirms that the spraying of cellulose nanofibre on the base sheet allows the complete retention of cellulose nanofibre. The laboratory spray coating confirms that this technique enhanced the barrier properties of the base sheet. For continuous spray coating of cellulose nanofibre on the base sheet, the dow web coater integrated with professional spray gun is used. In this experimental setup, the speed of the web controls the coat weight of cellulose nanofibre on the base sheet. Preliminary studies on dow web coater showed that spraying is a feasible technology to increase the barrier and mechanical properties of the base sheet.

3.7 Future Research:

This project proposes to investigate the development of spray coating process for fabrication of various cellulose nanofibre based functional materials such as barrier layers, coating on the base sheet, nano composite with Nano clay and cellulose nanofibre crystal. When compared to the conventional method for developing cellulose nanofibre materials, spraying could provide contactless coating with substrate and a contour coat applied to uneven surfaces.

Moreover, a tear sensitive web materials could be coated with spray system and coating weight can be controlled by changing the web velocities. Spray coating is a contactless coating process. The topography of the substrate has no influence on the coating weight. On uneven surfaces a contour coat can be applied; a closed film can be achieved with a decreased amount of liquid. This could result in a reduction of costs and an improvement of quality. The lack of a metering coating gap leads to a decreased sensitivity for coating defects and a reduction of web breaks - even for very low coating weights.

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4. Nanomaterials: Introduction and their Properties

Manish Kumar, Preetismita Borah

CSIR-Central Scientific Instruments Organisation,
Chandigarh, India.

Abstract:

Nanomaterials are natural products and may be generated through by-products of combustion reactions, or may be produced during engineering assignments for specific purposes. The chemical and physical properties of these nanomaterials are different to their counterparts of bulk mater. Nanomaterials sometimes may be produced by chance in the form of by-product of mechanical and industrial activities such as vehicle engine exhausts, smelting, welding fumes, combustion proceedings from domestic solid fuel heating and cooking. This chapter gives brief introducing from general information about nanomaterials, nanotechnology and later narrowing down to the concrete aspects of topic by placing emphasis on properties. This also deduces a short introduction of significance of nanomaterials properties in context of optical, thermal and sensing applications. Brief understanding of structure and properties of nanomaterials are also discussed. Nanotechnology includes controlling the size of materials at very small size that may be of 100 nanometers or lesser and also involves the manufacturing of instruments or materials in nanometer range. Nanotechnology is used globally in every field of engineering and science. Functionalized nanomaterials can promote the openings for engineering of structures to achieve modified properties.

Keywords:

Nanomaterials, properties, size, structure and applications.

4.1 Introduction:

Nobel laureate - Richard Smalley remarked as that future world would be magnificent due to the discovery of small atomic level things which will transform the human living style [1]. Nanoscience and technology will develop the new man made materials with changing their nature in coming years [2]. Physicist Richard P. Feynman suggested first time about 'nanotechnology' and advised that manufactured amenities and things would be with molecule features in coming era [3]. Feynman deduced an approach, such that a group with accurate apparatus can fabricate other small scale groups. In 1980s, Dr. K. Eric Drexler deeply elaborated the fundamental ideas, importance of nanotechnology and Nano devices through their speeches and books [4, 5].

It is well expressed about nanometer that this length scale is an amazing point where smaller fabricated device meets the natural atoms and molecules [6]. The size of nanomaterials remains bigger comparatively single atoms while lesser from bulk solids. As a comparison, other typical sizes of everyday objects and organisms [7] are shown in Figure 1.1.

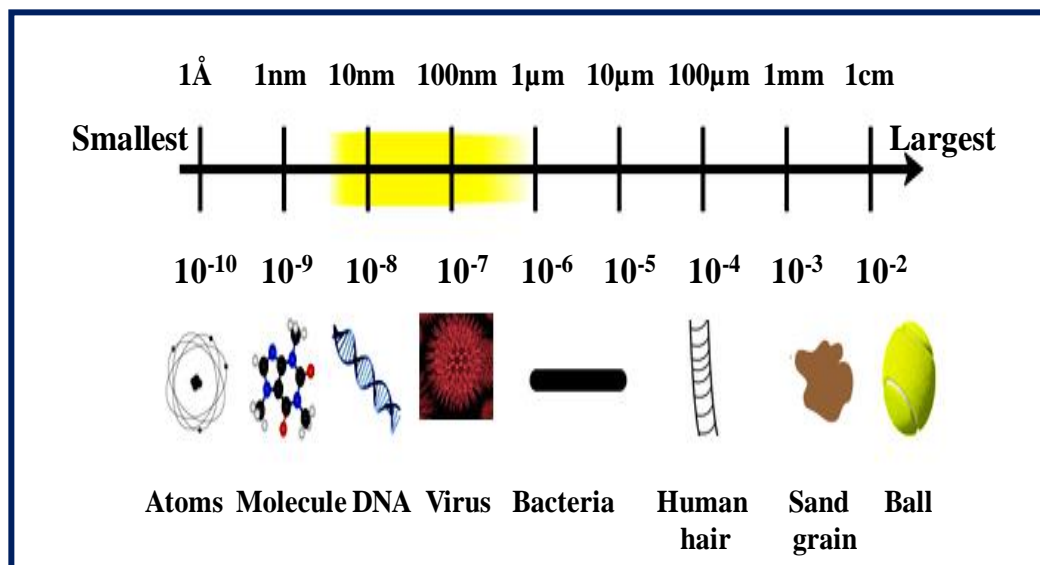


Figure 4.1: Size Regimes for Different Materials in Context To Nanometer

When size of materials decreases the physical, mechanical, chemical, thermal, optical and electronic features significantly changes. This is due to increasing dominance of atoms on the surface over that of those in the interior of the particle leading to alteration in their properties.

These properties of nanomaterials have evoked tremendous interest in the area of nanotechnology [8]. One nanometer is 10⁻⁹ m on the length scale and denotes about single molecule size [9]. The hair size (in wide) of human-being may be 60,000-80,000 nm so we guess that one nanometer is very small size.

4.2 Classification of Nanomaterials:

Nanomaterials are defined as particles (rods, crystals or spheres) having size in 1 and 100 nm range, at least in one dimension. Nanomaterials can be categorized based on its geometrical form and dimensionality of constituent elements [10], are shown in Figure 1.2.

- 0-D nanomaterials are in nanoscale ranges like nanoparticles.
- 1-D nanomaterials are above nanoscale ranges materials including nano-wires and nano-rods.
- 2-D nanomaterials are also above nanoscale ranges materials such as nano-sheets and nano-films.
- 3-D nanomaterials are not limited in the nanoscale includes bulk nanostructure materials or layers.

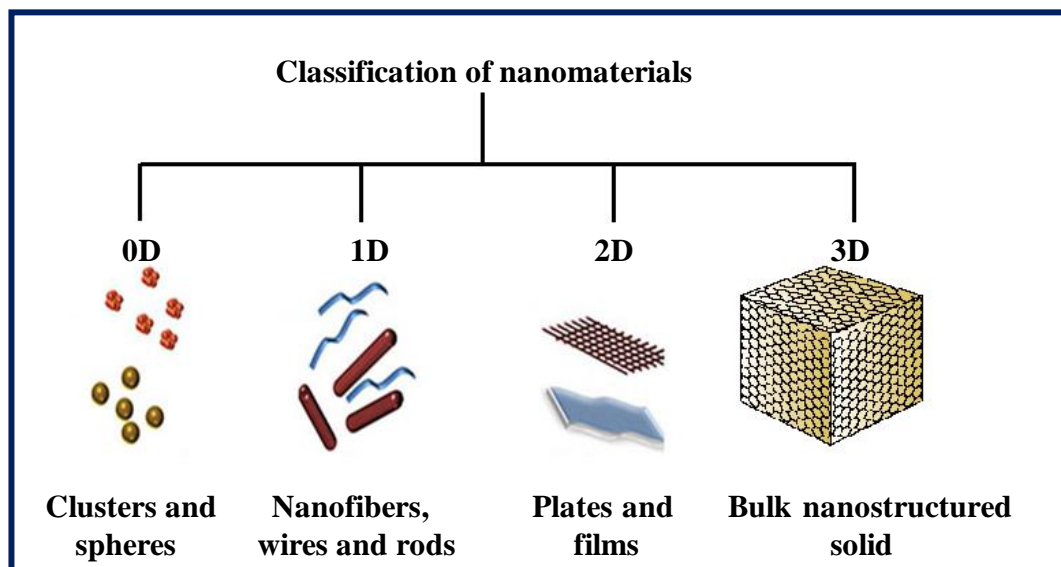


Figure 4.2: Different Forms of Nanomaterials on Dimension Basis

4.3 Categories of Nanomaterials:

Nanomaterials are further divided into four categories:

4.3.1 Carbon Structured Nanomaterials:

This type of nanomaterials is composition of carbon containing hollow spheres, cylindrical, ellipsoids or tubes configuration. Cylindrical carbon structures are known as nanotubes and ellipsoidal and spherical configured materials are referred to the fullerenes. Carbon based nanomaterials are stronger and lighter materials with beneficial uses in electronics area, improved films and coatings [11].

4.3.2 Metallic Nanomaterials:

Nano metals, oxides and quantum dots are included in these nanomaterials. Quantum dot crystal is formed of many atoms within the size of nanometer range. The size variation of quantum dots effects on the optical characteristic [12].

4.3.3 Dendrimers:

Nano sized polymers are the dendrimers which are made of bifurcate components. Dendrimer has number of chain-endings on their surfaces which are responsible for performing as particular role. Dendrimers possesses inner hollow chambers so that outer components may be settled in it. Thus, catalysis reaction is also completed with the help of these properties [13].

4.3.4 Nanocomposites:

Nanocomposites are combination of one, two or more components which contain superior features of every component individually. The nanocomposites may applied for investigation of physical, optical, electrical, thermal, barrier and flame retardant properties [14].

4.4 Approaches for Fabrication of Nanomaterials:

Nanomaterials are synthesized from two main approaches: top-down and bottom-up approach, expressed in Figure 1.3 [15]. In top-down approach, bulk molecule breaks down into its smaller parts by mechanical procedures. Bottom-up approach is subjecting molecule of precursor to various chemical routes and form different nanomaterials. Contamination and size control is the drawback of a top-down approach. Bottom-up approach minimizes some of these limitations.

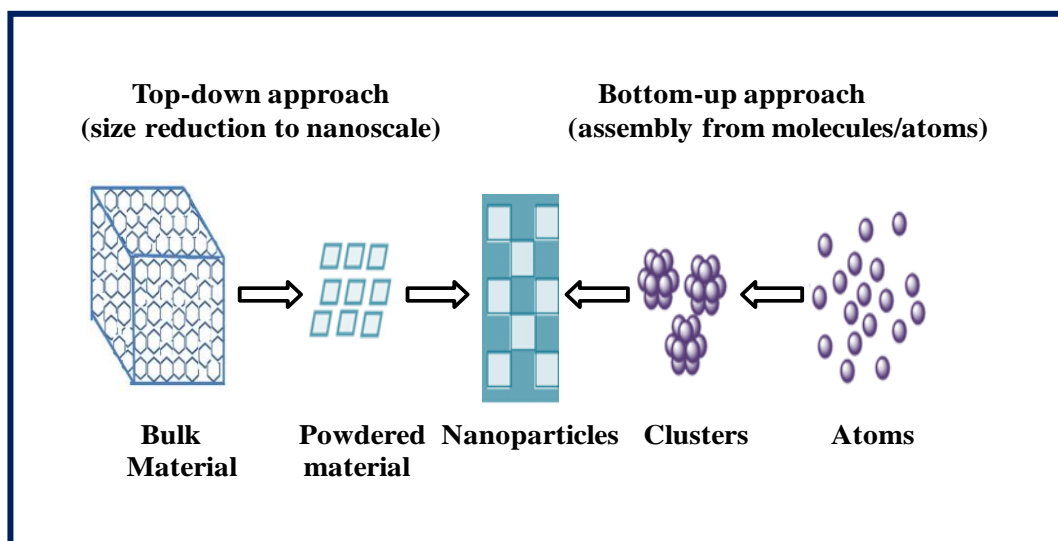


Figure 4.3: Approaches for Synthesis of Nanostructures

Bottom-up approach produces nanostructures with few defects, chemical composition with strong homogeneous and higher long and short ranges in order. While top-down approach involves internal stress with surface defects and contaminations. Nanostructures have been synthesized through various technologies and methods. The said approaches can be categorized in various groups.

They are synthesized whether from vapour, liquid or solid phase such that (i) vapour phase growth, involve laser reaction pyrolysis for synthesis of nanoparticle and atomic layer deposition (ALD), (ii) liquid phase growth, incorporate colloidal procedure for the preparation of nanoparticles and self-assembled monolayers, (iii) solid phase growth, include phase segregation to form nanoparticles in glass matrix and (iv) hybrid growth, contain vapour-liquid-solid (VLS) nanowires growth.

4.5 Shapes of Nanomaterials:

Metal particles are particularly interesting nanoscale system because of the ease with which they can be synthesized and modified chemically [16]. Nano sized metallic particles are unique and can considerably change physical, chemical, and biological properties due to their surface-to-volume ratio; therefore, these nanoparticles have been exploited for various purposes. These properties significantly depend on the size, shape and surface chemistry of the nanomaterials. Preparation and characterization of novel nanostructures (cubes, disks, plates, prisms, triangles, wires, rods and macroporous) of noble metals have come a long way of various investigations in the laboratories [17–21]. In recent years, new methods have been developed to synthesize non-spherical nanoparticles (Figure 1.4) like oval, cubic, rod, pyramid, etc. [22, 23].

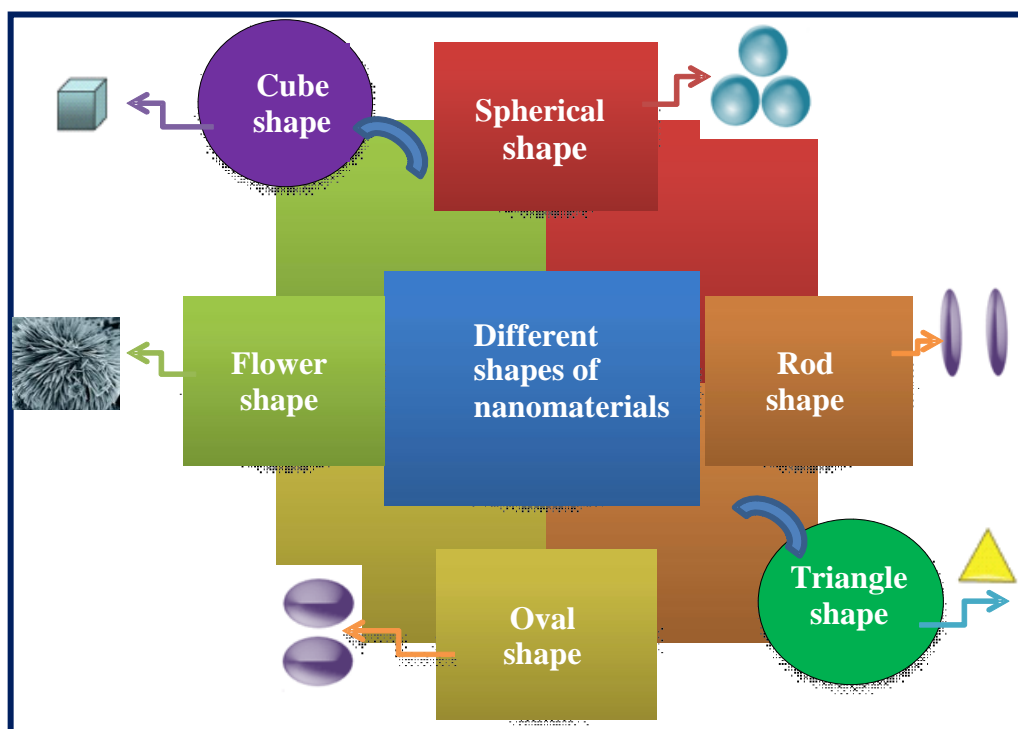


Figure 4.4: Representation About Different Shapes of Nanomaterials

4.6 Applications of Nanotechnology:

Unrivalled options are developing for re-engineered existing materials within 100 nm ranges like nanodots, crystalline materials, fibers (nanorods, nanotubes) and films which provide a better choice to fabricate further new nanodevices and materials [24]. Nanotechnology assigns various applications in optical, communication, electronics, biological systems and novel materials [25]. The applications of nanoparticles are depended on various factors like physical properties of material, size and surface area. Figure 1.5 shows an overview of various applications of nanotechnology.

As the sizes of the materials exist in nanoscale range, the surface atoms increase strongly along with increase in surface volume (S/V) ratio so that the material behaves like more chemically reactive. The performance of nanomaterials with quantum confinement, surface plasmon resonance (SPR) and super paramagnetism properties will improve day by day. So that, low cost and featured nanopowders, nanoparticles, and nanocomposites would be developed having broad applications.

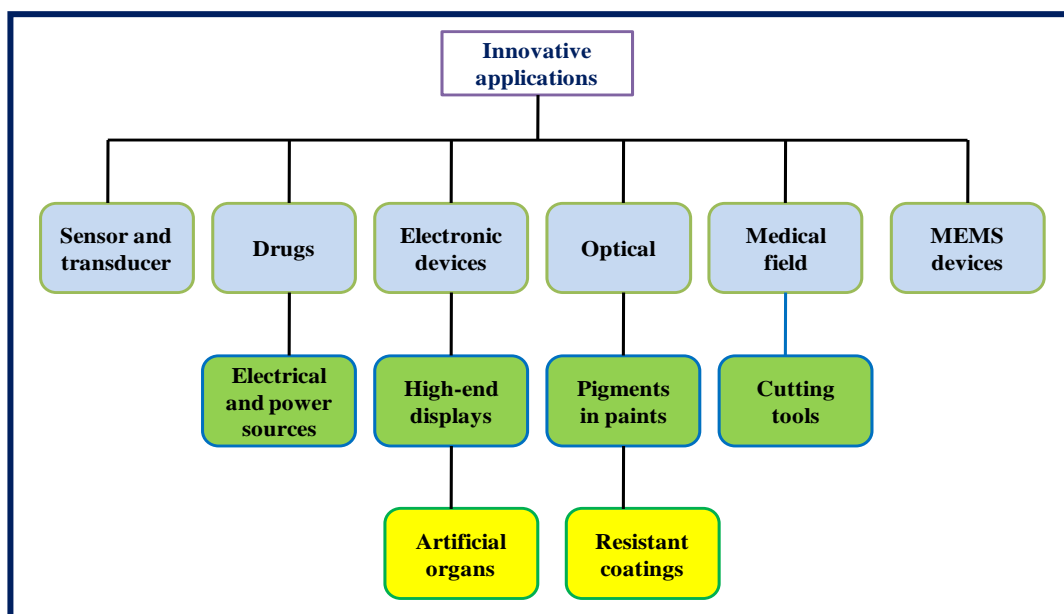


Figure 4.5: Applications of Nanotechnology in Various Areas

These nanomaterials will also apply in chemical and energy conversion procedures as highly selective and efficient catalysts. The nanomaterials functionalized catalysis may provide an importance in photo-conversion devices, bioconversion (energy), bio-processing (food and agriculture), fuel cell devices, waste and pollution control systems.

4.7 Some Properties of Nanomaterials:

Nanomaterials have been widely used due to the numerous applications for human being. The nanomaterials are within 100 nm ranges and possess 20 - 15,000 molecules. These nanoparticles contain different specific physical, chemical and biological valuable characteristic than own bulk substance.

4.7.1 Optical Properties:

The nanomaterials bands deduce a collective oscillation of conduction band electrons. The electrons match the sizes of silver nanoparticles are too smaller than the wavelength of incident light. Such, the constant electric field of incident light and the electrons generates an electromagnetic field which behaves as a surface plasmon resonance (SPR) [26]. The absorption/scattering effects may be modified with adjusting the parameters like size, shape

and refractive index for nanoparticles. As such, small nanoparticle absorbs light having peak about 400-420 nm, whereas bigger sized nanoparticle has enhanced scattering with broad band and shifts towards higher wavelength. Moreover, the changes in optical characteristics also possible by delocalization of particles aggregation and the conduction electrons [27]. These small sized silver nanoparticles can easily observe using conventional microscope due to its high scattering cross section. When silver nanoparticles irradiated from white source, produce bright blue color which is due to the SPR [28].

4.7.2 Thermal Properties:

Thermal behaviour is one of the significant properties of metal nanostructures. The thermal properties of nanomaterials are commonly determined by Thermogravimetric analysis (TGA) technique and theoretically it can be derived by Gibbs–Thomson. Thermal properties depend upon the size of nanoparticles due to the large S/V ratio while it is ignorable in case of bulk material. Previous studies stated that the melting point is found at low temperature for small sized nanoparticles [29]. The lower thermal conductivity value of nanoparticles suggests the existence of a stabilizer agent which capped the nanoparticles properly and prevents from further growth [30].

4.7.3 Electrical Properties:

Some nanomaterials with their unique electrical properties can be utilized in electronic devices. The electrical conductance of nanoparticles varying in size from 4 to 12 nm that were grown in glass-ceramic was examined [31]. The study found that the presence of these type of nanoparticles in ECAs decreased the resistivity. The above findings prove that nanomaterials have the potential to be exploited in electrical devices. The zeta potential (ζ) defines the electrical potential in colloidal dispersions to indicate the potential stability of nanoparticles [32]. A large negative or positive zeta potential of nanoparticles suggest that they tend to repel each other and there is no tendency to flocculate or vice versa.

4.7.4 Sensing Properties:

Nanomaterials show good sensing activity. Every sensing system has its merits and demerits and possesses an important role in the applicable area. For detection of volatile organic vapors, the performance of gas sensing depends on the S/V ratio of the materials. Nanomaterials have better sensing capacity than bulk or thin film sensors. A gas sensor can gather information about composition and concentration of any gas throughout the environment [33].

In the context of toxic gases, their concentrations may serve as biomarkers of disease in skin, blood, breathe and faces. To detect these gases for prevention form health problems, gas sensor has been developed. The sensing and determination of toxic gases are very important issue with great effect on the atmosphere, industries and medical area [34]. Gas detection in dense concentrations is easy to sensing due to its sharp odour. The quantification determination of some gas concentration is not possible by the human nose. Furthermore, it is possible to detect these type of gases at low concentration (<ppb in air) by sensing.

4.8 Summary:

In brief, this chapter has delivered the development in the recent years in synthesis approaches, properties, improvement with modifications and applications of nanomaterials. The complications came across by these materials in terms of crystal phases and nonstoichiometric compositions are cultivated. This chapter provides synthesis approaches and important characteristics of nanomaterials. The applications of nanomaterials in optical, electrical, sensing and thermal areas are discussed.

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5. Nanomaterials

Dr. D. Prakash

Assistant Professor,
Department of Physics,
Hindusthan Institute of Technology,
Coimabatore, Tamilnadu, India.

Dr. B. Yogeswari

Associate Professor,
Department of Physics,
Sri Eshwar College of Engineering,
Coimbatore, Tamilnadu, India.

5.1 Introduction:

Today, everybody is talking about nanomaterials, even advertisements for consumer products use the prefix “Nano” as a keyword for special features, and, indeed, very many publications, books, and journals are devoted to this topic. Nanomaterials is a new step in the evolution of understanding and utilization of materials. Material science started with the realization that chemical composition is the main factor in determining what a material is. Hereafter it was discovered that the fabrication and after fabrication steps could influence those properties substantially. Also small additives proved to be able to modify these properties. Finally, with the arrival of nanotechnology, it was discovered that the ability to create small particles could expand the capability to create and modify materials [1,2]. Nanotechnology is as well as evolutionary as revolutionary in nature. Evolutionary are the many applications where the same material is incrementally improved by using nanotechnology. Revolutionary it can be called where new (enabling) properties originate from nanotechnology like for example in quantum dots. Those new properties can be divided in:

- Properties based on the fact that the surface is large compared to the weight/volume.
- In addition to size, low energy dissipation and high processing speeds are important.
- New properties not found in bulk or micro sized particles.

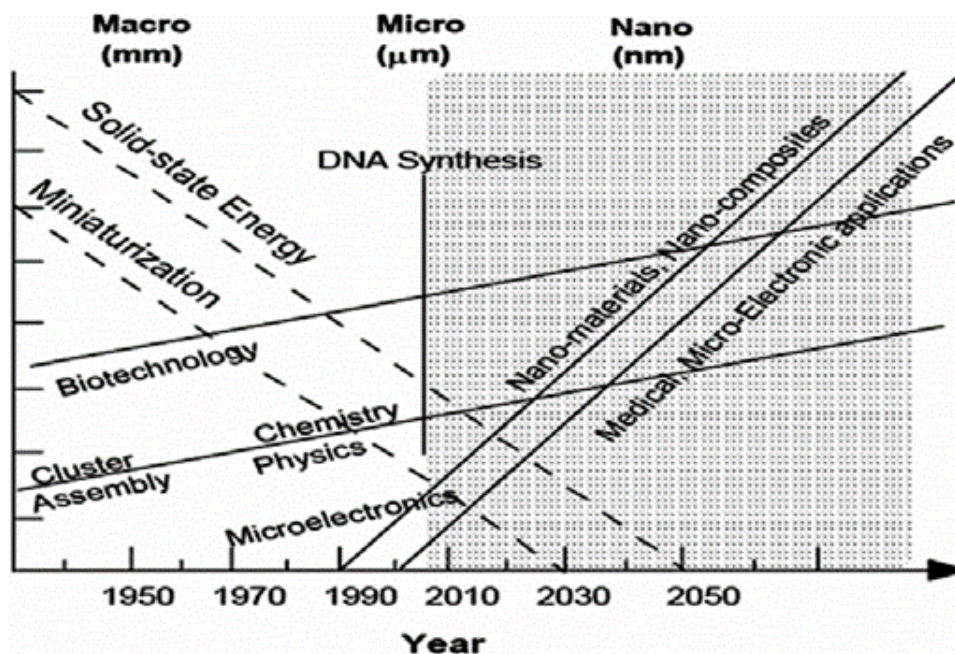


Figure 5.1: Evolution of Science and Technology and The Future

5.2 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.

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 (nanometer) 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 behaviour.

5.3 Main Differences Between Nanomaterials and Bulk Materials:

Two primary factors cause nanomaterials to behave significantly differently than bulk materials: surface effects (causing smooth properties scaling due to the fraction of atoms at the surface) and quantum effects (showing discontinuous behavior due to quantum confinement effects in materials with delocalized electrons) [3]. These factors affect the chemical reactivity of materials, as well as their mechanical, optical, electric, and magnetic properties.

5.4 Advances in Nanomaterials:

Today Nano phase 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.

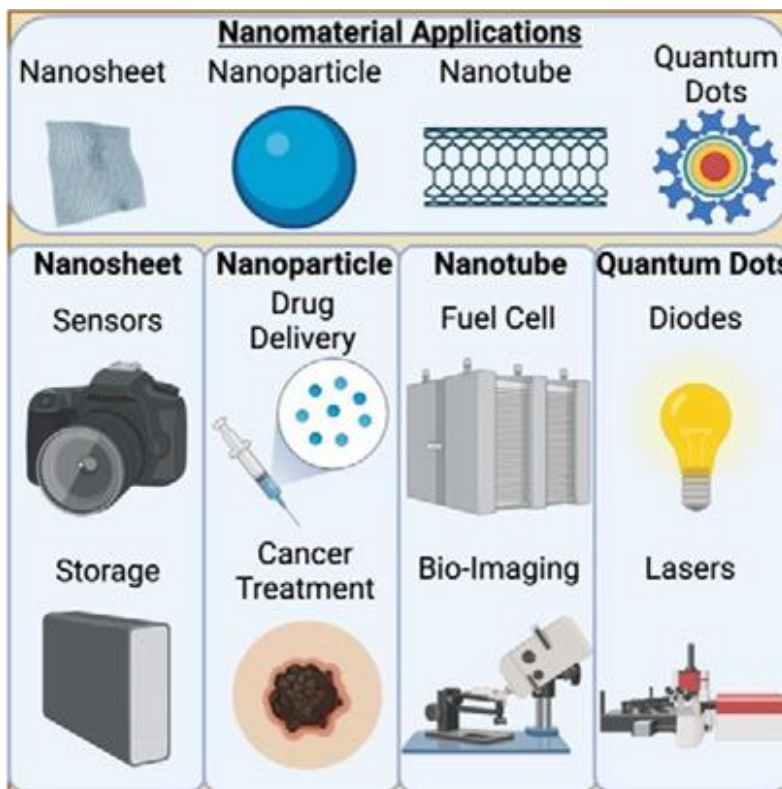


Figure 5.2: Advances in Nanomaterials

5.5 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:

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

5.6 Synthesis of Nanomaterials:

There are a large number of techniques available to synthesize different types of nanomaterials in the form of colloids, clusters, powders, tubes, rods, wires, thin films etc. There are various physical, chemical, biological and hybrid techniques available to synthesize nanomaterials. The technique to be used depends upon the material of interest, type of nanostructure viz., zero dimensional, one dimensional, or two dimensional material size, quantity etc.

- Physical methods: (a) mechanical: ball milling, melt mixing (b) Vapor: physical vapor deposition, laser ablation, sputter deposition, electric arc deposition, ion implantation
- Chemical methods: colloids, sol-gel, L-B films, inverse micelles. Biological methods: bio membranes, DNA, enzymes, microorganisms.

5.6.1 Physical Methods:

a. Ball Milling:

It is used in making of nanoparticles of some metals and alloys in the form of powder. Usually the mill contains one or more containers are used at a time to make fine particles. Size of container depends upon the quantity of interest. Hardened steel or tungsten carbide balls are put in containers along with powder or flakes (<50 μm) of a material of interest. Initial material can be of arbitrary size and shape. Container is closed with tight lids. The containers are rotated at high speed (a few hundreds of rpm) around their own axis. Additionally, they may rotate around some central axis and are therefore called as 'planetary ball mill'. When the containers are rotating around the central axis, the material is forced to the walls and is pressed against the walls. But due to the motion of the containers around their own axis, the material is forced to other region of the container. By controlling the speed of rotation of the central axis and container as well as duration of milling, it is possible to ground the material to fine powder whose size can be quite uniform.

Some of the materials like Co, Cr, W, Ni-Ti, AlFe, Ag-Fe etc. are made nanocrystal line using ball mill.

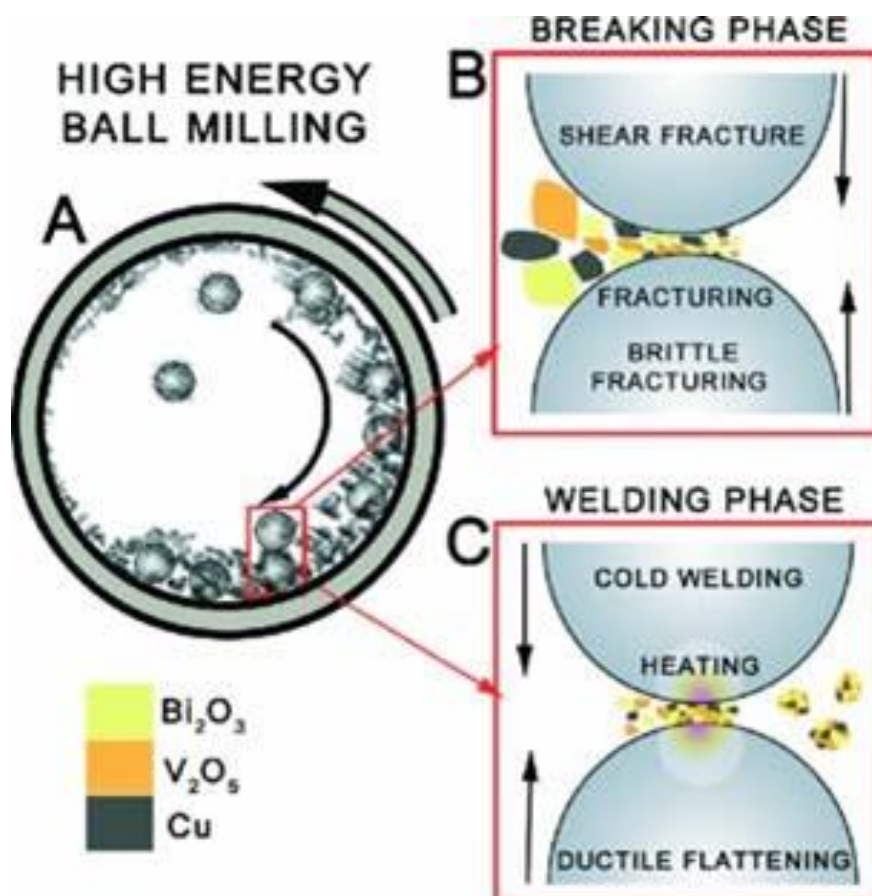


Figure 5.3: Schematic representation of the high energy ball milling synthesis mechanism for Cu- doped BiVO₄ nanoparticles

b. Melt Mixing:

It is possible to form or arrest the nanoparticles in glass. Structurally, glass is an amorphous solid, lacking long range periodic arrangement as well as symmetry arrangement of atoms/molecules. When a liquid is cooled below certain temperature, it forms either a crystalline or amorphous solid (glass). Nuclei are formed spontaneously with homogenous (in the melt) or inhomogeneous (on the surface of other materials) nucleation, which can grow to form ordered, crystalline solid. Usually, metals form crystalline solids but, if cooled at very high cooling rate, they can form amorphous solids. Such solids are known as metallic glasses. Even in such cases the atoms try to reorganize themselves into crystalline solids. Addition of elements like B, P, Si etc. helps to keep the metallic glasses in amorphous state. It is possible to form nanocrystals within metallic glasses. It is also possible to form some nanoparticles by mixing the molten streams of metals at high velocity with turbulence. On mixing thoroughly, nanoparticles are formed.

c. Physical Vapor Deposition:

It involves material for evaporation, an inert gas or reactive gas for collision of material vapor, a cold finger on which clusters or nanoparticles can condense, a scraper to scrape the nanoparticles and piston-anvil (an arrangement in which nanoparticle powder can be compacted). All the processes are carried out in a vacuum chamber so that the desired purity of the end product can be obtained. Metals or high vapor pressure metal oxides are evaporated or sublimated from filaments or boats of refractory metals like W, Ta, Mo in which materials to be evaporated are held. Size, shape and even the phase of evaporated material can depend upon the gas pressure in deposition chamber. Clusters or nanoparticles condensed on the cold finger (water or liquid nitrogen cooled) can be scraped off inside the vacuum system. The process of evaporation and condensation can be repeated several times until enough quantity of material falls through a funnel in which a piston-anvil arrangement has been provided.

5.6.2 Chemical Methods (Wet Chemical Route):

There are numerous advantages of using chemical methods, which are:

- Inexpensive, less instrumentation compared to many physical methods
- Low temperature (< 350 C) synthesis
- Doping of foreign atoms (ions) possible during synthesis
- Variety of size and shapes are possible
- Self-assembly or patterning is possible

5.6.3 Sol-Gel Method:

As the name implies sol-gel involves two types of materials or components 'sol' and 'gel'. There are several advantages of sol-gel: All sol-gel formation process is usually a low temperature process. This means less energy consumption and less pollution too. Some of the benefits like getting unique materials such as aerogels, zeolites, ordered porous solids by organic-inorganic hybridization are unique to sol-gel process. It is also possible to synthesize nanoparticles, nano rods, nanotubes etc., using sol-gel technique. Sols are solid particles in a liquid. They are thus a subclass of colloids. Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquid). A sol-gel process involves formation of 'sols' in a liquid and then connecting the sol particles (or some subunit capable of forming a porous network) to form a network. By drying the liquid, it is possible to obtain powders, thin films or even monolithic solid. Synthesis of sol-gel in general involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes. Precursors (starting chemicals) are to be chosen so that they have a tendency to form gels. Both alkoxides or metal salts can be used. Alkoxides have a general formula $M(\text{ROH})_n$, where M is a cation, R an alcohol group, and n is the number of (ROH) groups with each cation. Salts are denoted as MX, in which M is a cation and X is an anion. Although it is not mandatory that only oxides be formed by a sol-gel process, often oxide ceramics are best synthesized by a sol-gel route.

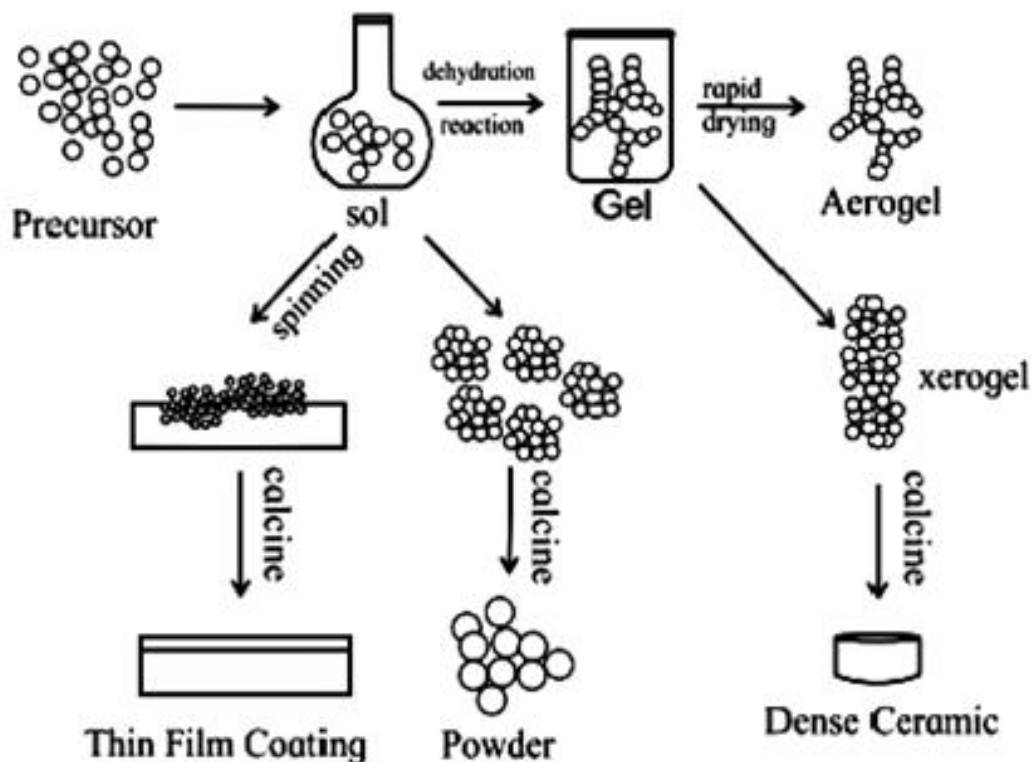


Figure 5.4: Schematic representation of the sol-gel process of synthesis of nanoparticles

a. Colloids and Colloids in Solutions:

A class of materials in which two or more phases (solid, liquid, gas) of same or different materials co-exist with at least one dimension less than a micrometer is known as colloids. Colloids may be particles, plates, or fibers. Nanomaterials are a sub-class of colloids, in which one of the dimensions of colloids is in about 1 to 100 nm range. Colloids are the particles suspended in some host matrix.

b. Microemulsion:

Synthesis of nanoparticles in the cavities produced in micro emulsion is a widely used method. Advantage of this method is the biocompatibility and biodegradability of synthesized materials. Biocompatibility is useful in drug delivery of nanomaterials and biodegradability is environmentally useful. Whenever two immiscible liquids are mechanically agitated or stirred together, they are known to form what is called 'emulsion'. The tendency of the liquids is such that the liquid is smaller quantity tries to form small droplets, coagulated droplets or layers so that they are all separated from the rest of the liquid (for example droplets of fat in milk). The droplet sizes in emulsion are usually larger than 100 nm up to even few millimeters. Emulsions are usually turbid in appearance. On the other hand, there is another class of immiscible liquids, known as micro emulsions which are transparent and the droplets are in the range of ~1 to 100 nm.

5.7 Unique Nanomaterial Features:

The properties of matter at the nanoscale level are substantially distinct compared to bulk counterparts. Size-dependent effects become more prominent at the nanoscale. For example, Au solution appears yellow when in the bulk and it appears purple or red at the nanoscale level.

The properties of nanomaterials can be tuned via tuning the nanomaterial size.^{92,93} At the nanoscale, the electronic properties are substantially changed compared to bulk materials.

The electronic properties of semiconductors in the 1–10 nm range are controlled by quantum mechanical considerations. Thus, nano spheres with diameters in the range of 1–10 nm are known as quantum dots. The optical properties of nanomaterials such as quantum dots strongly depend upon their shape and size [4].

Among a range of unique properties, the following key properties can be obtained upon tuning the sizes and morphologies of nanomaterials.

5.7.1 Surface Area:

The surface areas of nanomaterials are generally substantially high compared with their bulk counterparts, and this property is associated with all nanomaterials [5].

5.7.2 Magnetism:

The magnetic behavior of elements can change at the nanoscale. A non-magnetic element can become magnetic at the nanoscale level [6].

5.7.3 Quantum Effects:

Quantum effects are more pronounced at the nanoscale level. However, the size at which these effects will appear strongly depends upon the nature of the semiconductor material [7].

5.7.4 High Thermal and Electrical Conductivity:

According to the nature of the nanomaterial, extraordinary thermal and electrical conductivity can be exhibited at the nanoscale level compared to bulk counterparts. One example of this is graphene attained from graphite [8].

5.7.5 Excellent Mechanical Properties:

Nanomaterials exhibit excellent mechanical properties that are absent in their macroscopic counterparts [9].

5.8 Challenges and Future Perspectives:

Currently, huge numbers of theoretical and experimental literature studies of nanomaterials and nanotechnology have been witnessed. Future technologies depend upon how effectively materials can be manipulated on the nanoscale for various applications. However, at the same time, the development and effective utilization of nanomaterials involve many challenges. The dream of clean energy production is becoming possible with the advancement of nanomaterial based engineering strategies. These materials have shown promising results, leading to new generations of hydrogen fuel cells and solar cells, acting as efficient catalysts for water splitting, and showing excellent capacity for hydrogen storage. Nanomaterials have a great future in the field of nano medicine. Nano carriers can be used for the delivery of therapeutic molecules.

5.9 Conclusion:

In this chapter, the efforts have done to compile the small wonders of nanotechnology and that may be already be in our world and some that may be on the horizon. Nanomaterials are the building blocks of practical nanotechnology and can be physically and chemically manipulated for specific purposes. Nanomaterials play an important role in development of science and technology in various fields such as nano medicine, Nano biotechnology, green nanotechnology, industrial sectors and in reduction of energy consumption. Thus nanomaterials and nanotechnology are the current and future of the technology.

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6. One Step Combustion Method for The Preparation of 3n Pure (99.9%) Nano Alumina Powder for Substrate Making in Led Applications

Priyanka Nayar, Pooja Yadav, Paresh Nageshwar

Jawaharlal Nehru Aluminum Research Design and Development Centre,
Wadi, Nagpur, Maharashtra, India.

Upendra Singh, Anupam Agnihotri

Jawaharlal Nehru Aluminum Research Design and Development Centre,
Wadi, Nagpur, Maharashtra, India.

Abstract:

Alumina (Al_2O_3) is widely used in a variety of applications, because it has superior physical and chemical properties which is high heat resistance, excellent electrical isolation, abrasion resistance and high corrosion resistance. Generally, alumina is manufactured with a purity of 99.6 – 99.9% mainly by the Bayer process with bauxite as the starting material. It is used in refractory products; spark plugs and IC substrate and so on. High purity alumina, which has a purity of more than 99.99% and has a uniform fine particle has been widely used in translucent tubes for high-pressure sodium lamps, single crystal materials such as sapphires for watch covers, high-strength ceramic tools, abrasives for magnetic tape and the like. In recent years, the demand of high purity alumina is expanding in fields which are expected to show a high growth rate e.g., display materials, energy, automobiles, semiconductors and computers. In this paper we report the preparation of Nano-alpha alumina powders with a purity of 3N (99.9%) by two different chemical routes viz. auto combustion and alkoxide methods. XRD, BET surface area, SEM and ICP, TGA, LIBS were used to characterize the powders produced.

Keywords:

Nanomaterials, alumina, auto combustion, alkoxide route, SEM, ICP, XRD.

6.1 Introduction:

The natural sapphire is corundum (α -alumina) with traces of metallic elements that can impart a variety of colors including that found in the familiar blue sapphire (iron & titanium) and ruby (chromium). Production of synthetic sapphire has been possible for over a century (Verneuil, 1902 and Czochralski, 1916) but even as recently as a decade ago, annual world production was only a few hundred tones. The last decade has seen rapid growth in both production and new applications for synthetic sapphire based on a number of fundamental properties of corundum including its high electrical insulating and thermal conductivity properties and its well-known hardness of 9.0 on the Mohs scale. The starting material for

the production of synthetic sapphire is high purity alumina (HPA) which is usually accepted to be greater than or equal to 99.99% purity (4N or 100ppm impurities).

Al₂O₃ or alumina generally refers to corundum. It is a white oxide. Alumina has several phases such as gamma, delta, theta, and alpha. However, the alpha alumina phase is the most thermodynamically stable phase. Al₂O₃ in its α -phase is used as a good ceramic material which has many interesting properties, for example high hardness, high stability, high insulation, and transparency [1]. Alumina is also widely used in the fire retard, catalyst, insulator, surface protective coating, and composite materials [2-6].

Generally, Bayer's process is used for preparing the α -Al₂O₃ [7]. Alumina powder is available abundantly and at a low cost, hence it is a widely used material for making structural components, electronic devices, and substrates etc. There are several other methods of preparation of α -Al₂O₃ like pyrolysis [8], plasma evaporation process [9], sol-gel process [10], molten salt [11], hydrothermal [12], and solvothermal [13] techniques and so on.

These days, nano-sized alumina has attracted much attention due to large surface area in their nano-scale range rather than micron size. It has more applications in nano-matching and nano-probes [14]. The nano-size transition alumina [15] are used to obtain high-quality ceramics. The ceramics are used for the high temperature applications, drug delivery [16], absorbents, and soft abrasive coatings [17] applications. There are several other applications like, thin film or as a dielectric layer in electronic component industry, antireflective coatings [18], refractory, wave-guide sensors [19] and buffer layer [20] etc. It is also being used as nanoparticles in catalysis, as membranes and structural materials.

There are different phases of alumina such as:

- Cubic-spinel
- Tetragonal
- Monoclinic
- Cubic-spinel, and
- Alumina (orthorhombic) [21,22] and α -alumina.

From all the existing phases α -alumina, also called as corundum, is very common and thermodynamically stable [23]. Nano-size alumina is prepared by several techniques like sol gel [24], arc plasma [25] and re-condensation [26] etc. The most popular technique to make ultra-fine Al₂O₃ is sol-gel auto combustion and alkoxide routes because they are low-cost, low pollution and easy to be prepared on large scale.

In some of the previous work done on the preparation of alumina nano-particles is reported by different routes like micro-emulsions [27], microwave [28], sol-gel [29,30], hydrothermal [31-32], but there is no study reported on comparison of the phase transformed nano-particles due to variation in preparation conditions. The different intermediate phases of Al₂O₃ are very unstable and they can be converted to the most stable α -phase by controlling the heat treatment given through the combustion temperature or by increasing the annealing temperature.

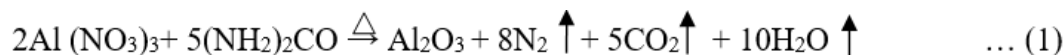
In this work more emphasis is given on the behavioral characteristic based on the phase transformation of nano-alumina by the stated two different preparation methods. It is very difficult to obtain the α -phase of alumina at temperatures below 1000° C, we accepted this challenge and tried to achieve it in this course of work.

6.2 Experimental:

6.2.1 Sol Gel Auto Combustion Synthesis:

In this method alumina was prepared by combustion, using metal nitrates as oxidizer and urea as a fuel [33,34]. Stoichiometric amount of pure aluminum nitrate nonahydrate (AR Grade, 99.99% purity) and urea were dissolved in distilled water to obtain a solution that was placed in constant stirring position on a hot plate at a temperature of 70-80oC for 4-5 hours.

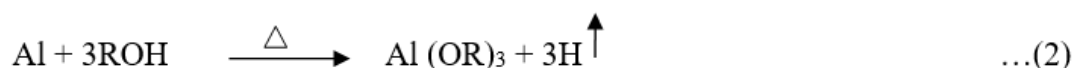
This resulted in a clear colorless transparent gel. A crucible containing the gel was inserted at 500° C in a preheated furnace. In few minutes the mixtures swell with evolution of gases and finally a flame appears. The flame lasts for about a minute. The crucible is removed from the furnace after the flame extinguishes. The foamy product is crushed to powder and used for further characterization. Following reaction took place for this process:



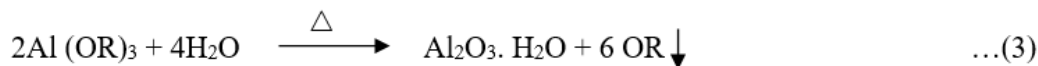
6.2.2 Alkoxide Route:

During this process, high purity aluminum alkoxide was synthesized from aluminum metal and alcohol, and hydrated alumina was produced by hydrolysis of alkoxide, and finally high purity alumina was formed.

For synthesis of alumina powder, 27 g of low-cost packaging grade aluminum foil was treated with 300 ml of anhydrous isopropyl alcohol (99.99% pure) under reflux, 0.2 gm of iodine was added as a catalyst and 1.6 gm of mercuric chloride dissolved in 40 ml of isopropanol and was released in reflux solution chamber after dissolution. After 1.5 hr excess of IPA was distilled out at 82°C and aluminum isopropoxide was distilled out at 135-140°C in gel form which was automatically dried at room temperature. The following reaction takes place with aluminum foil and isopropanol to form aluminum isopropoxide.



Preparation of aluminum isopropoxide was followed by its hydrolysis to get hydrated alumina. For this, 4 gm of dried aluminum isopropoxide was mixed with 15 ml anhydrous isopropanol and 15 ml distilled water and kept on stirring on a hot plate (70-80oC) for 6-7 hrs in a closed glass container. Sample solution was then filtered using Whatman filter paper. Obtained powder was oven dried (110oC) and then calcined at 1200oC to get pure alumina. Hydrolysis of aluminum isopropoxide was carried out by following reaction:



The as prepared Al_2O_3 powder obtained from both the methods was then crushed manually and taken for characterization as described in the following section.

6.2.3 Characterization:

X-ray diffraction measurements were performed on 3N pure alumina sample prepared by both the techniques (as mentioned above) using the Philips diffractometer in the grazing incidence geometry with Cu-K α radiations ($\lambda = 1.54056 \text{ \AA}$). XRD studies were performed by keeping the incidence angle fixed at 20° and scanning the scintillation detector in the 2θ range of 10° to 70° .

Impurity analysis of Minor elements present in sample was determined by Inductively Couple Plasma-Optical Emission Spectrometer (ICP); model ICAP-7400 Thermo Fisher Scientific at JNARDDC. Chemical analysis of alumina revealed the nature of minor impurity elements. The method adopted for sample preparation of ICP analysis is acid digestion as described below,

0.5 g of oven dried alumina powder sample was taken in a platinum crucible containing fusion mixture of H_3BO_3 & Na_2CO_3 in 1:3 ratios. Sample was then subjected to heat treatment at 1000°C in previously heated furnace for about one hour. Fused sample mass was then extracted with 1:1 HCL solution in hot condition & after dissolution & cooling, volume of alumina sample solution was then made up to 250 ml in a volumetric flask using ultra-pure water. Stock solution prepared was then analyzed for trace impurity by using ICP-OES and flame photometer. A blank solution was prepared to ensure any contamination. Table 6.1 gives the analytical methods for chemical characterization of alumina powder:

Table 6.1: Analytical method used for chemical characterization of alumina powder

Component	Chemical Characterization techniques
Na₂O	Fusion at 1000°C + HCL extraction of sample in hot condition followed by Flame Photometric analysis
Minor + Trace	Fusion at 1000°C + HCL extraction of sample in hot condition followed by ICP analysis

Surface morphology and homogeneity of the samples were examined using Scanning Electron Microscopy (SEM). Surface area of the prepared powders was easily determined using the Micromeritics ASAP 2020 gas adsorption analyzer and the application of the well-established BET method. AccuPyc II 1345 Pycnometer was used to calculate the density of alumina powder by measuring the amount of displaced helium gas. Thermo Gravimetric Analysis (TGA) was performed on alumina powders in air using a simultaneous thermal analyzer STA 409-PC Luxx in the temperature range between RT-1000°C at a heating rate of 10°C/min to verify the change in weight during conversion of phases at different temperatures. Thermographs provide information regarding the comparison of mass change with temperature for alumina sample.

The purity of the Al₂O₃ powder was analysed by using laser induced breakdown spectroscopy method. The Al₂O₃ pellet was made and the same is subjected to sintering at 1200°C. Finally, laser induced breakdown spectra of Al₂O₃ was recorded with different energy levels such as 5mJ, 10 mJ and 15 mJ respectively.

Al₂O₃ powder was subjected for thermal analysis with different time intervals such as 5, 10, 15, 20, 25 and 30 min. respectively to calculate the thermal conductivity as well as diffusivity.

6.3 Results and Discussion:

The as prepared Al₂O₃ nano-alumina powder was first taken for XRD characterization for confirming the phase formation during the sol-gel auto combustion method. Fig. 1 shows the XRD diffraction pattern taken on Philips X-ray Diffractometer in the grating incidence geometry with Cu- K α radiation ($\lambda=1.54056\text{\AA}$) compared with the standard α -alumina XRD pattern. It shows that there is an excellent match of the X-ray diffraction between both the patterns of lines corresponding to the same crystal structure.

There were no lines found which corresponds to the other phases of nano alumina, this satisfies that only single-phase nano alumina is obtained by the sol-gel auto combustion method at 450°C furnace temperature without any post annealing treatment. The XRD pattern does not changes even if the as prepared alumina powder is kept for annealing at the temperature say, 1000° C. Hence, these results show the formation of highly crystalline material α -alumina with a stable and irreversible phase.

The earlier studies show that nano alumina can be synthesized by SGAC process by initiating exothermic reaction with the mixture of urea + glycine as the fuel for exothermic reaction and produces the crystalline mixed phase [35].

Khorrani et.al. synthesized nano crystalline Al₂O₃ with sol-gel auto combustion and ultrasonic method but obtained γ -Al₂O₃ [36]. In another study it was reported that the complexing agent as citric acid which reduces the formation temperature to 750°C from 1000°C but yields the γ -phase of Al₂O₃ [37]. Roque et. al. prepared nano-alumina powder by combustion synthesis and got the FCC structure of the α -Al₂O₃ because of the excess of urea which restricts the complete oxidation of Al ions [38].

Figure 6.2 below shows the XRD pattern of alumina Nano powders prepared by alkoxide route. It is found that α -alumina was obtained by calcining hydrated alumina at high temperature of 1200°C after the rearrangements of oxygen packing. Ideally α -phase of alumina was obtained after calcination of hydrated alumina via different intermediate phases (γ , δ , θ etc).

Complete phase transition to thermodynamically stable phase of alumina strictly depends on the control of hydrolysis conditions as well as uniformity of temperature distribution during calcination [39]. Different researchers worked in order to lowering the transition temperature as below as 1000°C or even lower either by using seed crystals [40-42], or by adding elemental impurities [43].

On comparing the phase transformation of alumina nanoparticles prepared by sol gel auto combustion and alkoxide routes, it can be concluded that direct fuel combustion is needed to decompose aluminium nitrate with large amount of energy whereas in alkoxide route, calcination temperature of 1200°C is required to obtain α -phase of alumina that too with controlled conditions of hydrolysis, drying and calcination. Therefore, factors such as preparation methodology, precursor selection, annealing/combustion temperature, and time affect the crystallization properties of synthesized nanoparticles.

Figure 6.3 (a) and (b) shows SEM images with surface morphology of alumina nanoparticles prepared by auto combustion and alkoxide process respectively. Micrographs of 3N powder prepared by auto combustion process shows nano agglomerates which resulted in lower surface area whereas alumina formation by alkoxide route resulted in aggregates of crystallites that form network and chain like structure with high surface area and this kind of mesoporous structure could be suitable for various applications i.e. adsorption or catalysis etc.

Table 6.1 and 6.2 below shows the extent of impurities recorded by ICP-OES for the powder obtained by auto combustion and alkoxide route respectively. 3N pure alumina was clearly formed using both routes although minor trace impurities were observed in the one prepared by alkoxide method due to the distillation process used for the purification.

Table 6.2: Chemical Composition of alumina in traces prepared by auto combustion method

Alumina	Composition
Fe₂O₃	79.51 ppm
SiO₂	63.56 ppm
CaO	34.72 ppm
MgO	37.18 ppm
Na	0.028 %
Al₂O₃ (by diff)	99.95 %

Table 6.3: Chemical composition of alumina powder prepared by alkoxide route

Alumina	Composition
Fe ₂ O ₃	74 ppm
CaO	34.5 ppm
TiO ₂	0.5 ppm
Al ₂ O ₃ (by diff)	99.98 %

TG/DTA analysis of alumina samples generated by both the techniques were done to check thermal stability & change in weight with respect to increase in temperature. Fig. 4 show the TG behavior of alumina prepared via combustion method where negligible mass change was observed. Moisture was lost at 200°C. Endothermic peaks at 400°C and after 600°C were the result of evaporation of bonded water molecules. The overall mass loss for this sample was 1.55 %. Mass loss was found to be 0.92 % if we ignore the mass lost due to moisture. The reduction in mass loss was due to the high temperature generated during Auto combustion.

TG behavior of alumina prepared via alkoxide rout is as presented in Figure 6.5 below. From the thermograph it was found that after annealing alumina sample directly at 1200°C, bonded water molecules got evaporated therefore curve has not shown any mass change or endothermic peak.

Density of both the samples were determined using Helium gas displacement technique. Density values for alumina powder by both the methods are given in Table 6.4.

Table 6.4: Density of alumina powders

Property	Sample Combustion	Sample Alkoxide	Standard
Density (g/cm ³)	3.78	3.88	3.9

Highest density of 3.88 g/cm³ was achieved for the sample annealed at 1200°C although density values of both the alumina powders were very close to that of standard alumina (3.9 g/cm³) and found to be within the range of Sumitomo's high purity alumina (3.8-3.9). In order to use the above prepared alumina powder for the substrate making in LED fabrication, some of the characterizations were performed to test the powder for its spectroscopic and thermal properties.

Figure 6.6 shows the laser induced breakdown spectra of Al₂O₃ powder. From the spectra it is observed that along with Al and O, traces of Fe, Ca and Si element were also present in ppm range. Trichard et. al. reported the imaging of alumina support by laser induced breakdown spectra and found that LIBS can provide quantitative concentration including sulphur, vanadium and nickel in the ppm range. The report indicates that LIBS-based imaging represents a powerful tool for quickly providing two-dimensional elemental map over a large dynamic range i.e., typically from ppm to tens of percent [35].

Thermal conductivity and thermal diffusivity of Al₂O₃ powder at different time intervals of 5, 10, 15, 20, 25 and 30 mins are summarised in Table 6.5. The obtained results are in good agreement with previous literature [35]. These low values of conductivity and diffusivity are due to the presence of large number of pores in the powder and the absence of bonding between its particles. Solid alumina has a thermal conductivity 100 times higher than powdered alumina.

Table 6.5: Thermal properties of Al₂O₃ at different time intervals

Description	Thermal Conductivity (W/mK)	Thermal Diffusivity (mm ² /s)
Al ₂ O ₃ (5 mins)	0.2764	0.2666
Al ₂ O ₃ (10 mins)	0.2039	0.1793
Al ₂ O ₃ (15 mins)	0.2278	0.1749
Al ₂ O ₃ (20 mins)	0.2292	0.1801
Al ₂ O ₃ (25 mins)	0.2312	0.1819
Al ₂ O ₃ (30 mins)	0.2347	0.1959
Al ₂ O ₃ (35 mins)	0.24-0.30	0.15-0.30

6.4 Conclusions:

The proposed study was undertaken for comparing the properties (purity, structure and morphology) of alumina powder prepared by two different techniques. Although auto combustion method has an added advantage in obtaining the thermodynamically stable α -phase of 3N pure nano-alumina at much lower temperature, this technique is not cost effective due to the high cost of pure raw materials used. On the other hand, if we compare the particle size of the obtained alumina powder, combustion proves to be a better method for obtaining lesser particle size and low agglomeration which is a good property in substrate making. Also, if we compare the LIBS properties of the alumina powders prepared by both the methods, combustion method gives the better properties like minimum traces of impurities. In thermal conductivity and thermal diffusivity properties, the alumina powder prepared by combustion proves to give better thermal properties as required during the substrate making in LED fabrication techniques. Hence, on comparing both the methods of pure alumina (3N) preparation, auto combustion method proves to be a simple, one step, easy and useful for alumina powder preparation during the substrate making. This method does not require any post preparation annealing or sintering heat treatments to give phase pure and thermodynamically inert α -phase which resembles the actual corundum structure of the pure alumina (3N) powder.

6.5 Acknowledgements:

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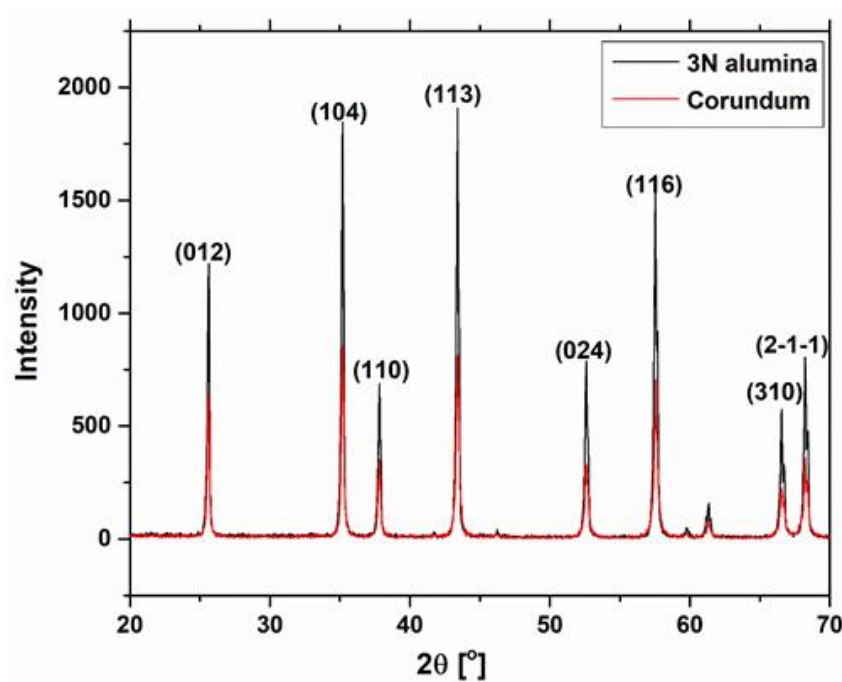


Figure 6.1: XRD Pattern of As Prepared Nano-Alumina by SGAC Method, Compared with Standard Calculated Data

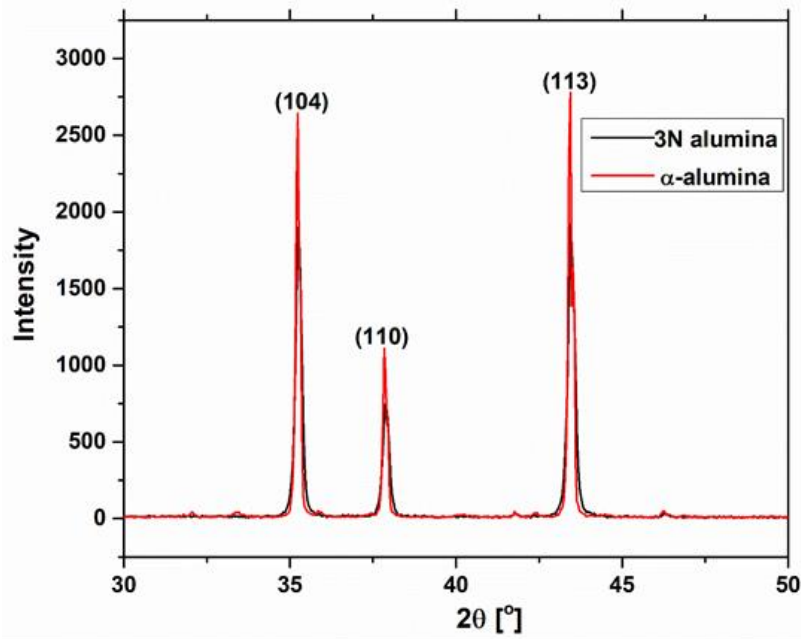


Figure 6.2: XRD Pattern of As Prepared Nano-Alumina by Alkoxide Method Compared with Standard Calculated Data

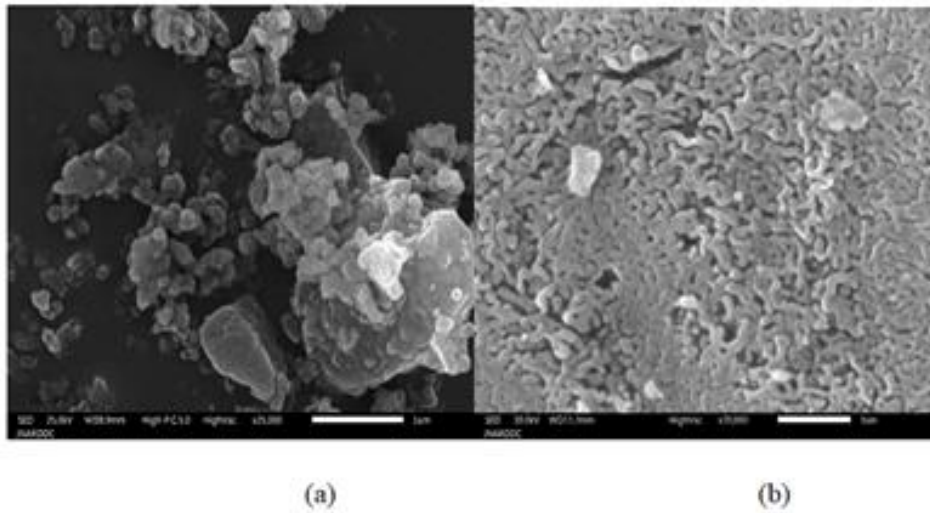


Figure 6.3: SEM Micrographs of
(a) Alumina Prepared by Sol Gel Auto Combustion and
(b) Alumina Prepared by Alkoxide Route

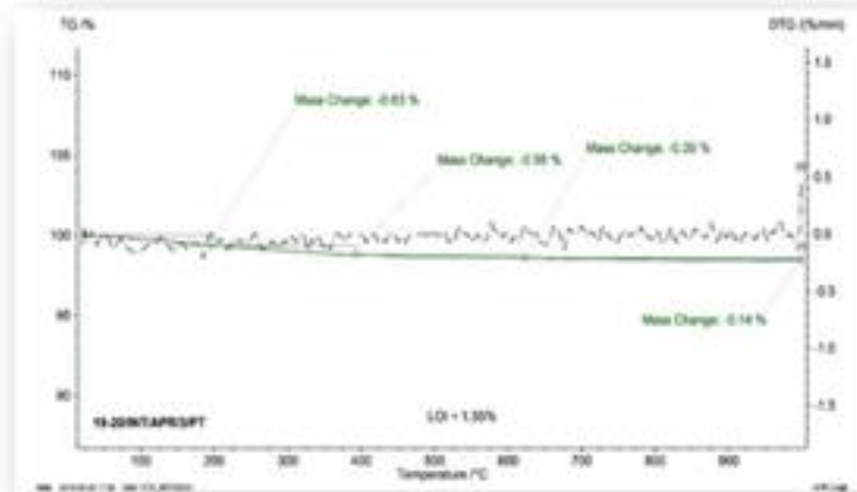


Figure 6.4: TG thermograph of Alumina Powder Prepared by Combustion Method

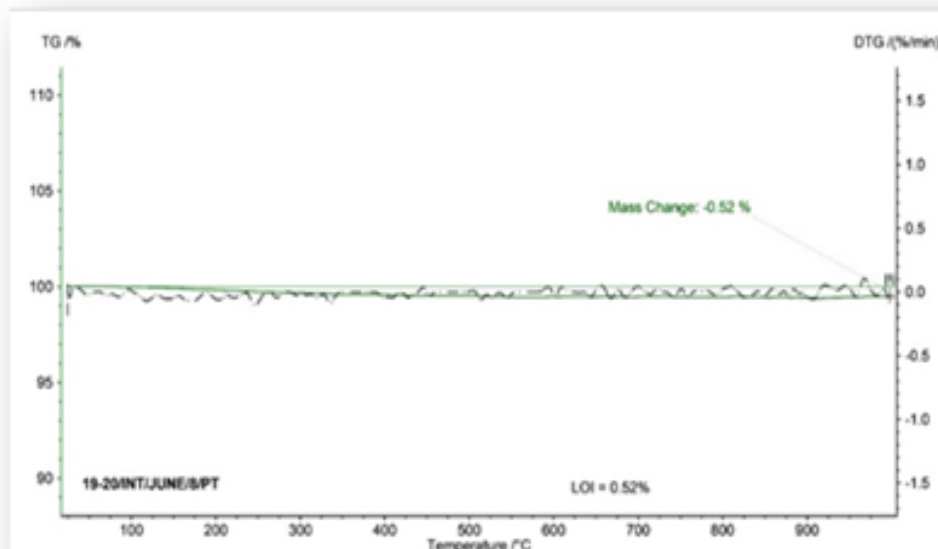


Figure 6.5: TG Thermograph of Alumina Powder Prepared by Alkoxide Method

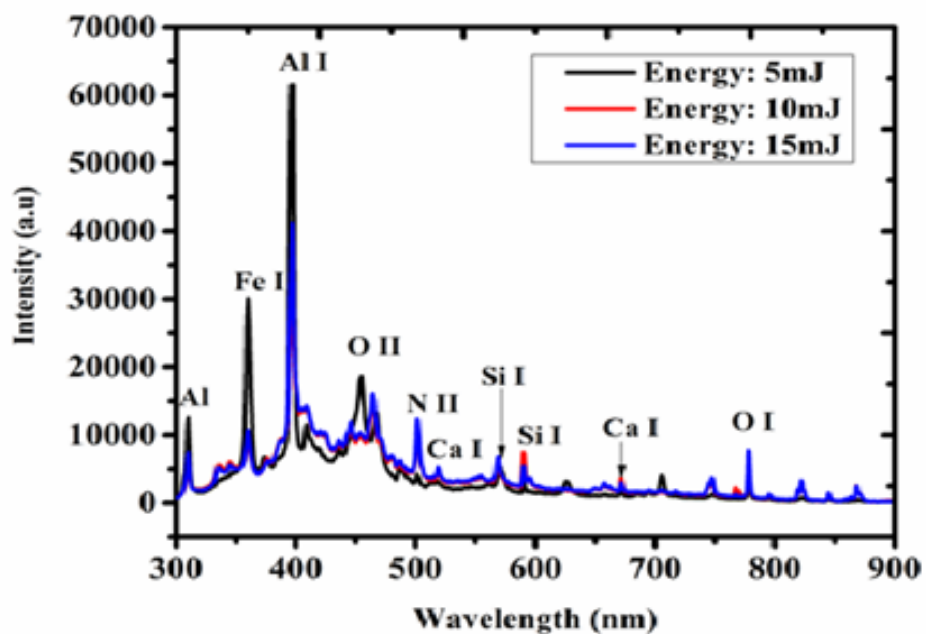
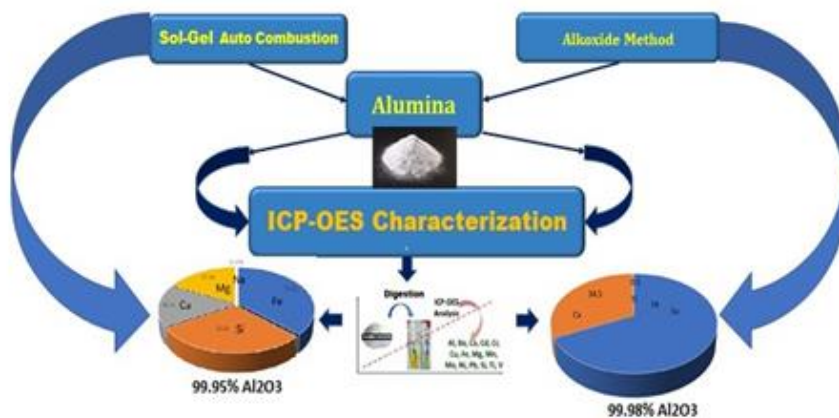


Figure 6.6: Laser Induced Breakdown Spectra of Alumina at Different Energy Levels



Graphical Abstract

7. Rare-Earth Zirconates ($\text{Ln}_2\text{Zr}_2\text{O}_7$): A Family of Ceramic (Nano) Materials

Melita Menelaou

Department of Chemical Engineering,
Cyprus University of Technology,
3036 Limassol, Cyprus.

7.1 Introduction:

Rare earth (RE) elements (or Lanthanoids) are a group of seventeen chemical elements in the periodic table: namely, fifteen lanthanides (Ln) or 4f elements ($Z = 57-71$), scandium (Sc) ($Z = 21$), and yttrium (Y) ($Z = 39$). The lanthanide series is the following: Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu). Scandium and Yttrium exhibit similar chemical properties as the lanthanides and thus they are altogether considered as rare earth elements. The first rare earth element which was discovered was Ytterbite (1787) from Lieutenant Carl Axel Arrhenius. Later, in 1800, Ytterbite was renamed to Gadolinite. Lanthanide chemistry has been extensively studied these last 3 decades, after the scientific community recognized that these elements have unusual physicochemical properties including fluorescent and magnetic properties. The main reason for these features is the presence of the 4f electrons which results in ligand-field effects for the trivalent ions. The electronic configurations of the lanthanides are $5d^16s^2$ for La, $4f^m5d^16s^2$ for Ce ($m = 1$), Gd ($m = 7$), and Lu ($m = 14$), and $4f^n6s^2$ for Pr→Eu ($n = 3-7$), and Dy→Yb ($n = 9-14$), respectively. Divalent lanthanides can therefore have the electronic structure $4f^{n-1}5d^1$, and trivalent lanthanides have a $4f^n$ configuration ($n = 0-14$).

Nowadays, scientists are preparing efficiently lanthanide-based materials for advanced applications; lanthanides are often referred to as “the seeds of technology” – a statement that highlights how important are the lanthanide-based materials for many technological purposes including solar cells, batteries, turbines, and lasers. Some years ago, the scientific community believed that only some of these elements had redox chemistry ($\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Ln}^{3+}/\text{Ln}^{2+}$ where Ln = La, Sm, Eu, and Yb). Nowadays, we know that all elements in this series have redox chemistry. Lanthanides are strong Lewis acids that can coordinate with hard bases (carboxylates) as well as highly electronegative donors (N or O) whilst coordination with water (or other solvents) is also often found.¹

The research community has recently shown an increased interest in a family of ceramic materials often called as rare-earth zirconates (or lanthanide zirconates or lanthanide zirconium oxides). The general formula of these materials is $\text{A}_2\text{B}_2\text{O}_7$ (where A = trivalent lanthanide ion, B = tetravalent transition metal ion such as Zr^{4+} , Ti^{4+} , Mo^{4+});² thus it is transformed to $\text{Ln}_2\text{Zr}_2\text{O}_7$ (or $\text{RE}_2\text{Zr}_2\text{O}_7$).

The increased interest for these materials is because of specific properties that render them excellent candidates for applications in the immobilization of radioactive waste,³ in thermal barrier coatings,⁴ and in photocatalysis.⁵ Rare-earth zirconates crystallize in the cubic structure at room temperature and at ambient pressures. Depending on the ionic radius ratio (RR) among the two metallic ions, $RR = r_{Ln^{3+}} / r_{Zr^{4+}}$, their structure can be stabilized with one of the two following space groups, either *Fd3m* (No. 227), which corresponds to the pyrochlore structure (P) (presence of large lanthanide ion), or *Fm3m* (No. 225) which corresponds to the defect-fluorite structure (F) (presence of small lanthanide ion).²

In particular, when the Ln element varies from Tb to Lu (when Ln = Tb→Lu), in the Ln₂Zr₂O₇ structure where the ionic radius ratio ranges from 1.44 to 1.35, these materials crystallize in a defect-fluorite structure.² Compounds Ln₂Zr₂O₇ (where Ln = La → Gd) with the ionic radius ratio to range from 1.61 to 1.46, then these materials adopt the cubic pyrochlore structure.²

The final annealing temperature can also be a crucial factor for the final structure. Their crystallographic structure contains two different cation sites and two distinct anion sites. Namely, the large trivalent lanthanide ions (Ln³⁺) occupy the eight-fold oxygen coordinated A sites, and the six-fold coordination of the B sites is filled by the smaller tetravalent zirconium ions (Zr⁴⁺) and 1/8th of the oxygen positions is vacant.

Thermally, upon application of pressure and/or chemical doping, pyrochlore structure can transform to the fluorite one. In particular, the 'P' structure can be considered as being derived from the 'F' structure by removing one eighth of the anions in such a way that the vacancies constitute a diamond sublattice (Figure 7.1).⁶

Many of these phases undergo a high-temperature order-disorder (P→F) phase transformation at elevated temperatures (1530–2400 °C),⁷ which has a strong influence on their physicochemical properties. The characteristic peaks that always, make the pyrochlore form diverse from the fluorite phase are (3 3 1) and (5 1 1). Among the rare-earth zirconate pyrochlores, there is a subgroup called defective pyrochlores such as the case of Gd₂Zr₂O₇ which show an incompletely disordered atomic array at ambient condition.

Pyrochlore materials show ionic, electronic, or mixed conductors and unusual magnetic properties. Doping with divalent cations such as Mg²⁺, Ca²⁺, Ba²⁺ and Sr²⁺ at the A site, and/or trivalent cations at the B site, can introduce further oxygen vacancies and increase protonic conductivity.

At high temperature (>1500 °C), Ln₂Zr₂O₇ materials (when Ln = Nd→Gd), undergo an order-disorder transition from a 'P' to a structure 'F' structure. The transition temperature depends on the nature of the rare-earth ion. Thus, lanthanum zirconate (when Ln = La) exists only in the pyrochlore structure, whereas for neodymium, samarium, and gadolinium zirconates, the transition from a pyrochlore to a fluorite structure occurs at 2300, 2000, and 1530 °C, respectively.^{2a} More recent studies however have proven that the lanthanide zirconate with a pyrochlore structure is not stable at high pressure and it undergoes a pressure induced structural transformation to a monoclinic phase (space group *P2₁/c*),⁸ or to a defect cotunnite-type structure (space group *Pnma*).⁹

7.2 Synthetic Methodologies of $\text{Ln}_2\text{Zr}_2\text{O}_7$:

Synthesis is the most important step in solid-state chemistry research and in materials science. Samples may be prepared in various as single crystals, polycrystalline powder, or a thin film. The physicochemical, thermal, and magnetic properties and therefore the applications of such materials depend significantly on the chemical composition, the shape and size of the particles, as well as the morphology.

All these factors are dramatically influenced by the applied synthetic methodology to obtain the rare-earth zirconates. Different wet chemistry approaches have been introduced for the synthesis of rare earth zirconates (Figure 7.2 and 7.3).¹⁰ All wet chemistry methods involve mixing of reactant precursors at the molecular level, thus better compositional homogeneity and stoichiometric control is achieved. The most common synthetic techniques are mentioned below.

7.3 Solid State Synthesis:

Solid-state synthesis (or the ceramic method) is frequently used to form a chemical reaction from solid starting materials (salts, metal oxides, etc) to form a new solid with a well-defined structure. End products include polycrystalline materials, single crystals, glasses, and thin-film materials that are widely used for energy and electronic applications among others.

Modern preparation techniques for solid state are not limited to variations on the ceramic method and many reports exist in the literature to support the technical details during preparation. The general procedure includes mixing of the zirconium source (usually in the form of ZrO_2 or ZrOCl_2) and the lanthanide oxide (Ln_2O_3) powders at high temperature under Ar atmosphere for long period of time (i.e. 10 hours).

The temperature should be in accordance with the nature of the lanthanide ion. The next step is calcination (or sintering) of the obtained powders at high temperatures for long duration of time in order to obtain $\text{Ln}_2\text{Zr}_2\text{O}_7$ ceramic materials.¹¹ Typical characterizations of such materials includes techniques such as XRD and SEM.

7.4 Coprecipitation:

Coprecipitation method is a classical and perhaps the simplest approach for synthesizing materials. The size, morphology, and composition of the as-prepared material can be controlled by a series of experimental parameters, such as the type of precursors, the precursor ratio, the surface ligand (if present), the reaction temperature, and the pH. In a typical coprecipitation method, an aqueous solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in presence of ammonia ($\text{pH} > 8$) lead to the formation of precipitation of metal ions in the form of hydroxide. Further, calcination is required at high temperature and for long duration of time in order to finally prepare the $\text{Ln}_2\text{Zr}_2\text{O}_7$ structures.¹² Through coprecipitation homogeneous materials with high purity can be obtained. In case of large grain-sized powders, an additional milling step may be necessary.

7.5 Hydrothermal/Solvothermal:

During the hydrothermal/solvothermal synthesis, the precursors are dissolved in a suitable solvent, and then transferred to an autoclave or a sealed glass tube. Usually the pressure is controlled by the gas law [$P = f(T)$], even though the pressure of some reactors can be controlled.

The pH adjustment (typically $\text{pH} > 7$) is achieved through the addition of a base agent such as ammonium hydroxide or sodium hydroxide. The hydrothermal/solvothermal synthesis is the only method that requires lower reaction temperature (typically 200-400 °C) compared to the above-mentioned methods and uses water as solvent or other common organic solvents.

For example, Hongming and Danqing prepared lanthanum zirconates by hydrothermal method using lanthanum nitrate, and zirconium nitrate salts, as well as NaOH to adjust the pH at 11. The hydrothermal reaction was completed at 200° C in 1 hour.¹³

7.6 Sol-Gel:

Sol-gel is another technique to synthesize of ceramic materials such as metal oxides, nitrides, and carbides. This is a simple, low-cost technique and environmentally friendly technique where Ln₂Zr₂O₇ materials with high sintering capacity can be synthesized under low reaction temperatures with good composition control, and high purity level. Very well-known porous structured materials such as zirconia or yttria-stabilized zirconia can be prepared under this technique.

The reaction mainly occurs by hydrolysis and condensation of a precursor resulting in the formation of a sol that, after a series of chemical reactions and/or mild thermal treatments, turns into a gel. The final material is obtained after calcination.¹⁴

7.7 Other Techniques:

7.7.1 Combustion:

Combustion method involves a simple reaction between fuel agents such as citric acid, glycine and hydrazine and metal precursors (oxidants). For example, lanthanum zirconate was synthesized by Matovic et al. by dissolving first La(NO₃)₃·6H₂O and zirconium chloride in glycine; then the prepared solution was heat-treated at 950 °C for 120 minutes and finally sintered at 1600 °C for 4 hours. This method helps to produce porous pyrochlore powders with high efficiency and uniform morphology.¹⁵

7.7.2 Floating Zone:

In the floating zone growth, the molten zone is kept between two vertical solid rods and a single crystal is grown by dipping a seed crystal into one end of the zone and translating the molten zone toward the feed stock.

The main advantage of this technique is the absence of the container, which precludes a contamination by the crucible material and the generation of crystal defects caused by the interaction between the growing crystal and the container.¹⁶

7.8 Application of Ln₂Zr₂O₇ Ceramic Nanomaterials – Thermal Barrier Coatings:

Complex oxides such as the rare-earth zirconate ceramic materials in the ‘F’ and/or ‘P’ structure display a variety of interesting and promising physical, chemical, thermal and magnetic properties which render them excellent candidates in applications such as photocatalysis, magnetism, solid electrolytes in high-temperature fuel cells and thermal barrier coatings, among others.

The performance of these materials in applications largely depends on their crystallinity, size, shape and surface structure. In addition, these ceramic materials display high thermal stability, chemical resistance, high thermal expansion coefficients, high melting points, low thermal conductivities, great ionic conductivity, and high sintering rate among others.

Nowadays, there is an increasing demand in energy efficiency and power generation and that is why the development of new technologies and advanced materials using environmentally friendly approaches and cost-effective production systems, appears mandatory.

Any significant technological step towards this direction, is immediately associated with the energy goals of the EU; namely, this is one out of five priorities based on the new EU energy strategy.¹⁷ High-temperature gas-turbine engines are nowadays widely used to generate a huge amount of energy (land-based turbines) and transport (aerospace gas-turbines).

One of the challenges for the industrial and gas-turbine engines for today's scientists, is to unravel the technological know-how in order to reduce both fuel consumption and pollutants emissions.¹⁸ Another significant challenge is to increase the operating temperature of the engines to a maximum temperature during operation and, at the same time, guarantee that the metallic parts of the turbines are not overheated.¹⁹

One suggestion on addressing these scientific and technological challenges is based on the optimization of the engine design; modelling and prediction tools are necessary to estimate parameters such as the turbulent flow, combustion chamber flow, position of internal cooling channels in lines and blades, and heat transfer.

Another suggestion is dedicated on the materials which cover both the combustion chamber and blades as Thermal Barrier Coatings (TBCs).²⁰ TBCs are the most effective and advanced ceramic systems for the protection and isolation of the hot section parts of turbine engines that allow higher combustion temperatures and thus, they can improve the efficiency of gas-turbine engines.²¹

Typical TBC structures (100 μm to 1 mm in thickness) for gas-turbine engines comprise of a bond-coat (typically made of MCrAlY; where M=Ni, Co, or a mixture of Co/Ni), a thermally grown oxide (TGO), and a ceramic top-coat; a TBC being deposited onto a metallic substrate (Ni-based superalloy). In some cases, the bond-coat may also consist of more than one layer, each of different chemical/phase composition.²² Currently, yttria-stabilized zirconia (7-8% of Y₂O₃-ZrO₂; YSZ) is the principal ceramic material used as top-coat layer for TBCs in high-temperature sections of aircraft gas-turbine engines.²³

This is due to the desirable properties of YSZ. Namely YSZ has a high melting point (~ 2700 °C), one of the lowest thermal conductivity ($\sim 2.3 \text{ Wm}^{-1}\text{K}^{-1}$ at ~ 1000 °C), a high thermal-expansion coefficient (CTE) ($\sim 11.10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), and good thermal and chemical stability.²⁴

However, YSZ-based TBCs (YSZ-TBCs) which are exceptional materials face severe limitations since the expectations regarding the TBC temperature capability continue to increase: the maximum surface temperature for conventional YSZ-TBCs is limited up to 1200 °C. Above 1200 °C, changes are observed in phase composition, microstructure and properties, which altogether are associated with high thermally-induced stresses. We can say that the existing YSZ-TBCs have reached the limits in terms of temperature capability.

In addition, YSZ-TBCs are subjected to a variety of aggressive environments leading to coating degradation due to ingestion and infiltration of calcia-magnesia-alumino-silicate (CMAS) environmental attack.²⁵ CMAS resistance can be achieved by adding one or more layers. Hence, there is the urgent need to develop the next generation of advanced Thermal and Environmental Barrier Coatings (TEBCs) using environmentally friendly and inexpensive deposition techniques which can combine desirable properties of YSZ and reach today's demands for higher temperature capabilities, high performance and significantly reduced degradation under severely aggressive environments. Among various requirements, these systems must have low thermal conductivity ($0.5\text{-}1 \text{ Wm}^{-1}\text{K}^{-1}$), phase stability at high temperatures, CTE close to that of the metallic substrate ($>9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), chemical compatibility with the underlying YSZ and appropriate CMAS resistance. Advanced ceramic materials can play the key role. The replacement of the metallic components of the existing systems seems less promising.

The development of advanced ceramic systems in a multilayer architecture, seems to be the most promising strategy to achieve the full potential of advanced ceramics.

Over the last decade, strategies have been proposed to replace YSZ to overcome the limitations of conventional TBCs.^{24b} However, due to the specificity and selectivity of YSZ for TBCs, all strategies had limited success.

Thus, a new opportunity arises now to discover new materials in the form of multilayer TBCs. For this purpose, rare-earth zirconates of pyrochlore and fluorite structure,²⁵ can be promising candidates. A typical example of such ceramic materials is lanthanum zirconate (LZ) (pyrochlore structure of La₂Zr₂O₇; Ln=La) and its properties (i.e. lower thermal conductivity than YSZ; $1.5\text{-}1.8 \text{ Wm}^{-1}\text{K}^{-1}$ at ~ 1000 °C, no phase transformation, CMAS resistance)²⁶ suggest that this material has many advantages when compared to YSZ.

Thus, LZ can act as top-coat layer(s) (LZ_x; x refers to a single layer or more layers) in multilayered architecture. The coating architecture and properties depend significantly on the ceramic materials used for the coatings.

Multilayer TBCs which comprise of advanced LZ_x top-coat layers and the currently prominent material YSZ as a middle layer, can provide a promising multilayer TBC candidate system (MCrAlY-YSZ-LZ_x) suitable to overcome the limitations of the conventional TBCs (MCrAlY-YSZ).

7.9 Conclusion:

Rare earth zirconate ceramic nanomaterials represent a class of materials with interesting physicochemical, magnetic, thermal, and optic properties. Altogether they lead to potential technological applications spanning from photocatalysis, magnetism, and nuclear waste storage, to solid electrolytes in high-temperature fuel cells and thermal barrier coatings.

This chapter describes the basic physicochemical features of these materials as well as the most common synthetic methodologies to obtain them. The last section of this chapter covers one significant potential application of the rare-earth zirconates which is the thermal barrier coatings.

Figures and Figure Captions:

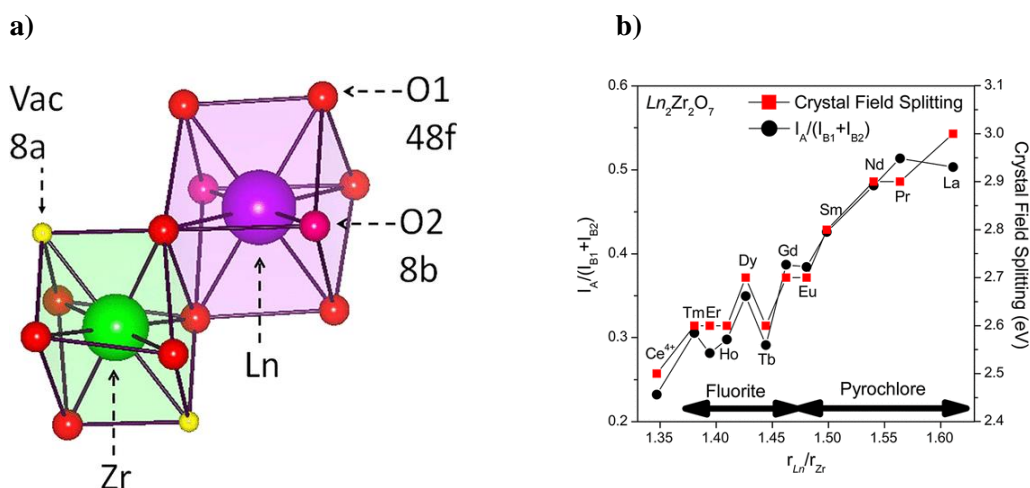


Figure 7.1: (a) Representation of the pyrochlore structure showing the relationship to the fluorite structure. In the fluorite the 8a sites are fully occupied, and (b) Plots of the crystal field splitting (ΔE) and the intensity ratio of features A and B ($I_A / (I_{B1} + I_{B2})$) as a function of r_{Ln} / r_{Zr} . Peak intensities are taken as the area of the peaks. (Reproduced from Ref. [6] with permission of the American Chemical Society).

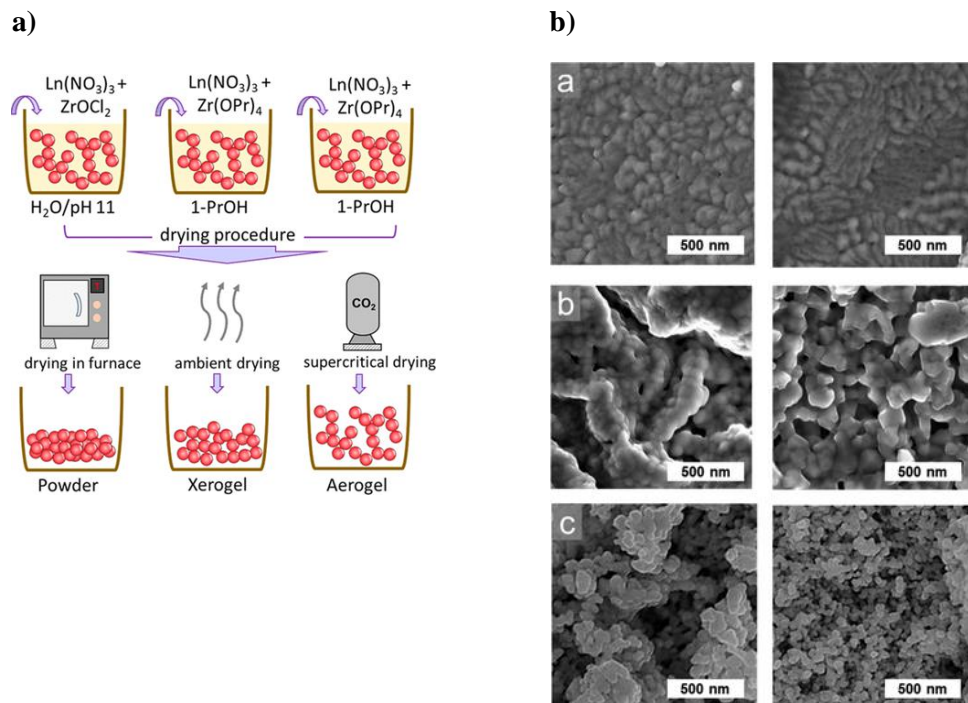


Figure 7.2: (a) Schematic representation of $Ln_2Zr_2O_7$ nanostructured materials prepared using different drying protocol and (b) Scanning electron microscopy: surface morphology of the calcined $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ (i) powders, (ii) xerogels, and (iii) aerogels at 1000 °C/5 h. (Reproduced from Ref. [10a] with permission of the American Chemical Society).

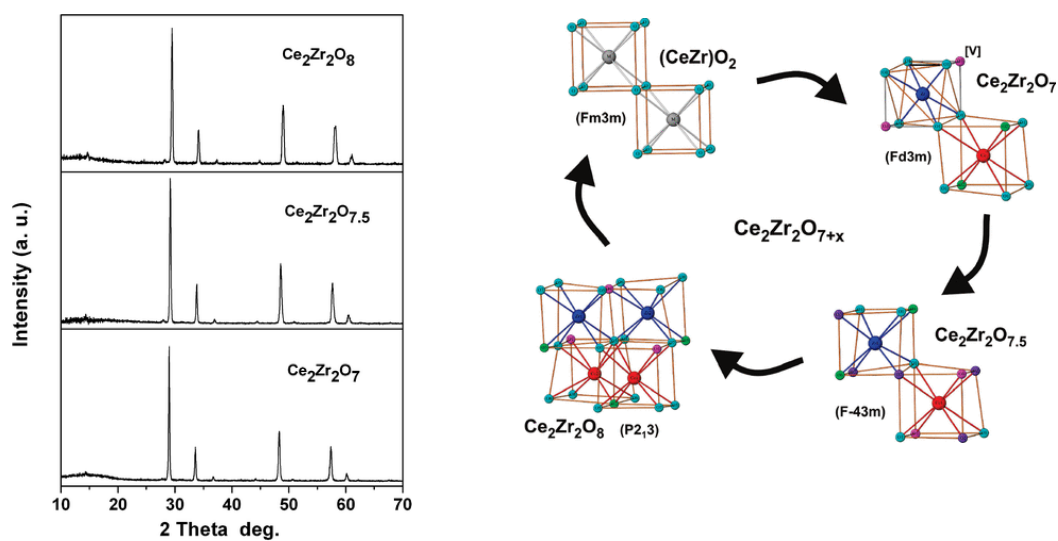


Figure 7.3: (a) Powder XRD patterns and (b) structural transformations in $Ce_2Zr_2O_7$, $Ce_2Zr_2O_{7.5}$, and $Ce_2Zr_2O_8$, respectively. (Reproduced from Ref. [10b] with permission of the American Chemical Society).

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8. Self-Assembly

Dr. Sanjeeb Sutradhar

Assistant Professor (Guest Faculty),
IKG Punjab Technical University (Main Campus),
Department of Chemical Sciences & Technical Consultant,
Scientech Laboratories, Inc. NJ, USA.

Dr. Soumyakanta Prusty

Assistant Professor,
Department of Chemistry,
Vellore Institute of Technology,
Andhra Pradesh.

8.1 Introduction:

Self-assembly is a ubiquitous phenomenon in biological as well as non-biological systems. By this process, the smaller individuals seemingly organise into ordered structure, without the intervention of any external sources.¹ This can be understood from its two components. The first component *i.e.* self indicates that “spontaneous process” and the second component *i.e.* assembly indicates that “association, aggregation or forming together”. Therefore, self-assembly of nanostructure is an assembly process that atoms, molecules or building block of nanoscale materials spontaneously organize into highly ordered structure or pattern in the nanoscale region without intervention from external sources. Nanoscale structure self-assembly occurs due to presence of supramolecular interactions between the individual components such as van der Waals, ionic, hydrophobic, hydrogen bond and coordination bond. The presence of these fundamental interactions in the individual components makes it highly ordered structure upon establishing the equilibration between assembly or non-assembly state of the individual component. These structures are currently well understood and can be controlled in order to get the desired functional properties of the self-assembly nanostructures.²⁻³ The synthetic strategy is pretty much similar to the synthetic strategy of micro/macro and nanoscale materials.⁴ The major aim of this book chapter is to illustrate the self-assembly of gold nanoparticles with different organic moiety assisted and its next-generation applications in biomedical as well as in electronics.

8.2 Small Organic Molecule Assisted Self-Assembly of Gold Nanoparticles:

Fullerene is a carbon cluster molecule and hydrophobic in nature. It has to be functionalize in order to make it hydrophilic in nature by introducing heteroatom like oxygen and nitrogen. One way to functionalize with well-known Prato reaction and synthesize N-methylfulleropyrrolidine derivative. This N-methylfulleropyrrolidine derivative was mixed with synthesized citrate capped gold nanoparticles with a certain ratio and assembly was increases with increasing the ratio *i.e.* the ratio of concentration of N-methylfulleropyrrolidine derivative to the concentration of citrate capped gold nanoparticles. This assembly was occurred due to interparticle charge transfer-induced and

governed by van der Waals interaction. The fullerene-C₆₀ surface contains 8 ring of pyrrolidine moiety and can extend the ordered structure in all possible direction upon equilibration established (*cf.* **Figure 1**). This assembly was pH tuneable and observed at 5.0-6.8 only.⁵ It was also investigated with 3-mercaptopropanoic acid for assembly process of this fullerene-C₆₀ derivative and was observed the similar phenomena.⁶ Nucleophilic addition reaction strategy can be used for functionalization of fullerene-C₆₀ with 1-methylpiperazine and synthesized 1-(4-methyl)-piperazinyl fullerene (MPF). This would be hydrophilic in nature and neutral molecule. This functionalized fullerene derivative can generate positive charge on the nitrogen of 1-methylpiperazine moiety with tuning the pH of the solution medium. The citrate capped gold nanoparticle possess negative charge on its surface ligand. This mixing of these two in certain ratio can harvest highly ordered 3-dimensional architecture. This assembly process was pH tuneable.⁷⁻⁸

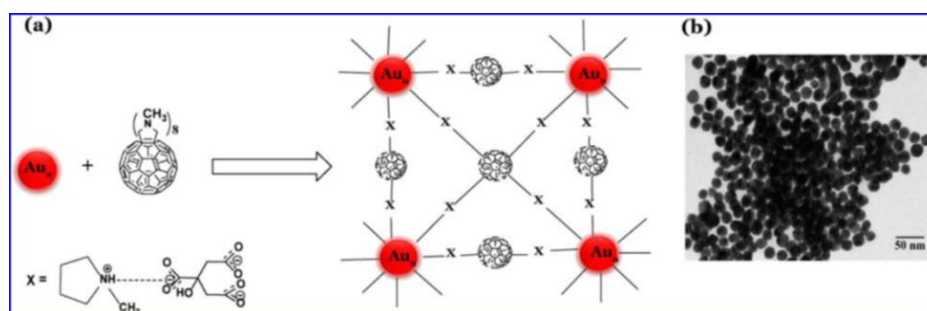


Figure 8.1: The interparticle interaction between N-methylfulleropyrrolidine derivative with citrate capped gold nanoparticles (a). The TEM micrograph of the corresponding assembly structure (b). Reprinted with permission from Ref. 5. Copyright 2007 American Chemical Society.

An interparticle linking agent tetradentate thioether, the *tetra*-[(methylthio) methyl] silane Si(CH₂SCH₃)₄ (TTE) was found to be assist for novel spherical assembly of gold nanoparticles. Tetraoctylammonium bromide capped gold nanoparticles were assembled due to interaction of tetradentate thioether and ligand place exchange reaction with dodecanethiol did not harvest the assembly structure, instead dis-assembly would be occurred. It did not observe any assembly of dodecanethiol capped gold nanoparticle with the tetradentate thioether. This indicated the assembly is ligand directed process and suitable chemical moiety should be present in the chemical structure of the ligand.⁹ Homocysteine is an amino acid containing thiol, amine, and carboxylic group in the chemical structure. The thiol will oxidize to increase the stability of nucleation process of gold nanoparticle and surface layer would be present amine and carboxylic acid group for tailoring the assembly process. It was established that the driving process for assembly was due to interaction of negative charge on oxygen of one homocysteine capped gold nanoparticle with the positive charge of nitrogen of another homocysteine capped gold nanoparticle (*cf.* **Figure 2**).¹⁰ In all the small organic molecule assisted gold nanoparticle assembly is characterized by decrease the absorbance of surface plasmon resonance at 520 nm and gradual evolution of increased absorbance at greater wavelength than surface plasmon resonance. Additionally, the physical appearance *i.e.* colour of the suitable ligand capped gold nanoparticle was also changes with assembly process. It was also estimated that interparticle distance by density functional theory (DFT) calculation and found to be 3.23 Å.⁵

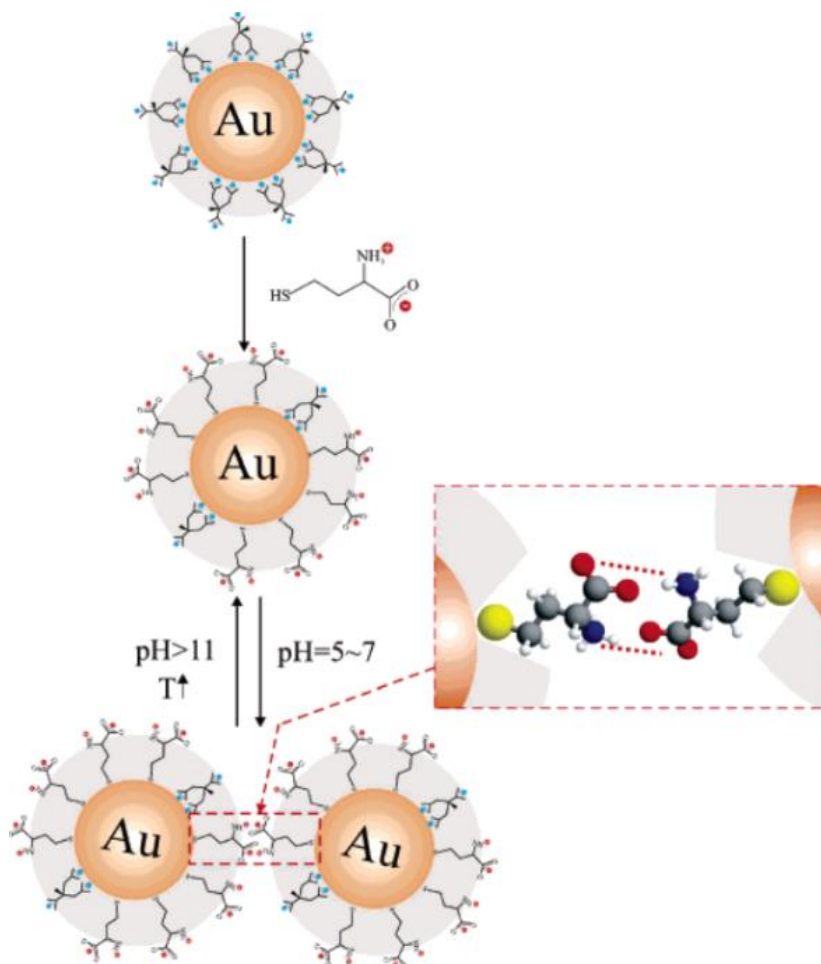


Figure 8.2: The interfacial interaction between the homocysteine capped gold nanoparticles. Reprinted with permission from Ref. 10. Copyright 2007 American Chemical Society.

8.3 Polymer Assisted Self-Assembly of Gold Nanoparticles:

Polymers are multiples of simple chemical monomers. The various functional moiety on to the polymer can be introduced in order to functionalize. The functionalized polymer can be polarized or generate charge by chemical modification or tuning the pH of the medium and can act as a source of binding site of ligand capped gold nanoparticles. The linear and periodic polymer has alternating ionic and polar sequences in the dilute concentration of polymer. The periodic polymer consist of alternated cationic poly-L-lysine (PLL) blocks and polar sequences of poly (ethylene glycol) (PEG) of varying chain length was used as a linking agent to assemble the 11-mercaptoundecanoic acid capped gold nanoparticles (*cf.* **Figure 3**). It was taken the advantage of positive charge on polymer side chain and negative charge on the monolayer of 11-mercaptoundecanoic acid capped gold nanoparticles.¹¹ The azo-benzene has ability for cis-trans isomerization due to $\pi-\pi^*$ transition and can be tuneable with the application of ultraviolet (UV) light. The trans-isomer can't induce

assembly process due to presence of phenyl ring on either side and on the other hand *cis*-isomer induces assembly process due to increased shell polarity and thereby switches the solubility. The azo-benzene moiety can be introduced chemically into the polymer structure along with reversible addition–fragmentation chain transfer-(RAFT-) polymerization using 2-cyano-2-propylbenzodithioate as a control agent. The citrate capped gold nanoparticle would undergo ligand place exchange reaction with azo-moiety containing polymer and under UV light (365 nm) the polymer shell on to the gold nanoparticle changed structure from *trans* to *cis*. This *cis* transformation assisted in the formation of assembled structure and could be easily identified by the UV-visible spectroscopy. The assembled structure sedimentation would occur and could easily be identify by comparing the *trans*-isomer absorbance and *cis*-isomer absorbance.¹² The wrinkles as an external template can be used as linking agent for the assembly process due to their excellent scalability and high precision. The gold nanoparticle can also be used for assembly process but it is less colloidal stable due to aggregation during the drying process. This instability can be overcome by functionalizing the gold nanoparticle surface such as poly(N-isopropylacrylamide) (PNIPAM), poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT/PSS), poly(vinyl pyrrolidone) (PVP), poly(ethyleneglycol) (PEG) layers, and bovine serum albumin (BSA) protein layer.¹³ The dodecanethiol-stabilized gold nanoparticles were assembled during the polymerization reaction between diglycidylether of bisphenol A (DGEBA) and dodecylamine (DA) due to presence of dodecyl chains in both components. This allowed to stabilize due to strong hydrophobic-hydrophobic interaction. The desorption of dodecanthiol from gold nanoparticles has taken place followed by coalescence of nude gold nanoparticles to produce larger sized gold nanoparticles with narrow size distribution of the nanoparticle. This phenomenon could be attributed from the broadening of the absorption spectra to the red shift. The diglycidylether of bisphenol A (DGEBA) and dodecylamine (DA) precursor can be used for self-assembly of other suitable nanoparticle containing long alkyl chain for interaction stability.¹⁴

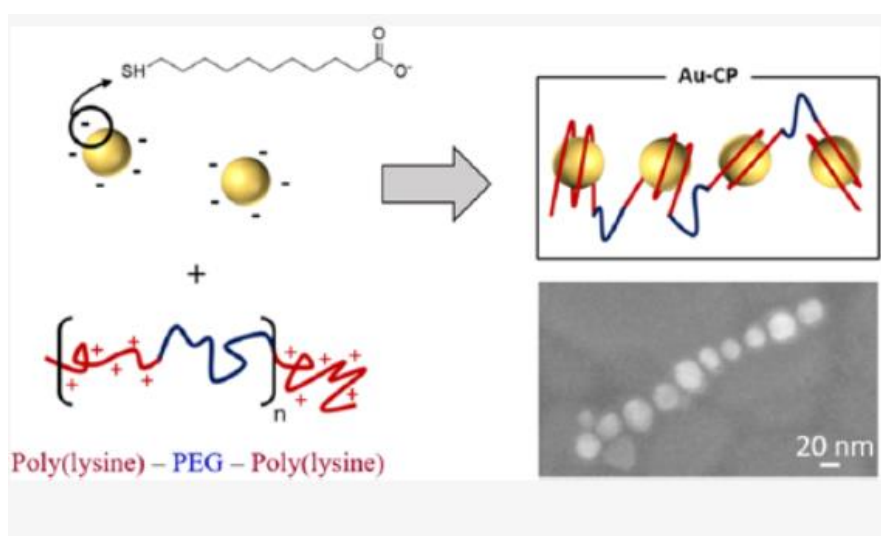


Figure 8.3: Assembly strategy between functionalized periodic polymer and 11-mercaptoundecanoic acid capped gold nanoparticles. Reprinted with permission from Ref. 10. Copyright 2020 American Chemical Society.

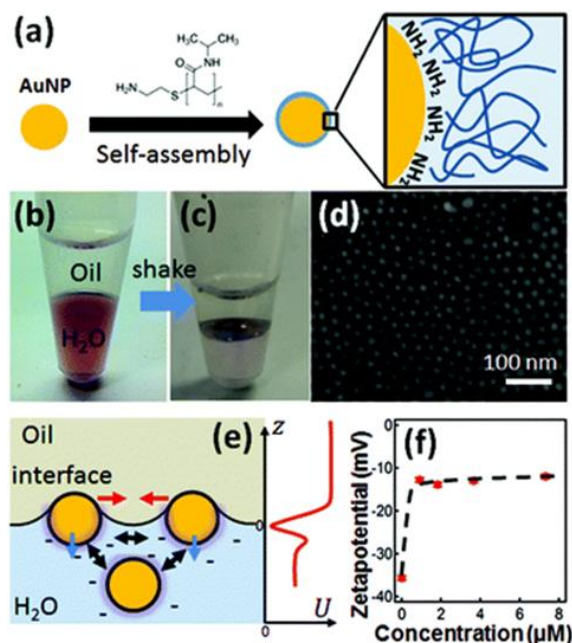


Figure 8.4: Strategy for polymer assisted gold nanoparticle assembly (a) and their colour changing from non-assembly state (b) to assembly state (b) with their corresponding SEM image. The interaction forces near the liquid-liquid interfaces *i.e.* capillary and van der Waals attraction (red), electrostatic and steric repulsion (black), solvation and line tension (blue), red curve (right) (d). The zeta-potential with the variation of concentration of gold nanoparticle assembly (f).¹⁵

The temperature induced assembly of gold nanoparticle was achieved by using amine terminated Poly-N-isopropylacrylamide polymer. It was well established that this polymer has temperature responsive characteristics. It was taken this characteristics advantage for self-assembly of citrate capped gold nanoparticle and could accelerated the process by cooling and heating for several cycles in order to get the thermodynamic equilibration with the aqueous phase. The addition of hexadecane solvent helped in precipitate out the gold nanoparticle at the liquid-liquid interface through vigorous shaking. The decrease of surface charge by using poly-N-isopropylacrylamide could replace the citrate ligand from the gold nanoparticle was evident from the zeta-potential study (*cf.* **Figure 4**).¹⁵

8.4 Surfactant Assisted Self-Assembly of Gold Nanoparticles:

A variety of surfactants have been used for the controlled synthesis of gold nanostructures owing to the presence of different head groups, hydrophobic chains, counter ions, and unique molecular structures. The critical micelle concentration (CMC) plays a critical role for the controlled synthesis of gold nanostructures which can be defined as the minimum concentration above which the micelles start to form. The siloxane surfactants are amphiphilic in nature with methylated siloxane hydrophobe coupled with one or more polyoxyethylene (EO) polar groups. This amphiphilic nature assisted in stabilising gold nanoparticles and also induced the gold nanoparticle assembly due to presence of one or more polyoxyethylene (EO) polar groups. It was believed that mechanism of formation

self-assembly proceeded in two steps *i.e.* first step is the formation of amphiphilic surfactant stabilized gold nanoparticle and second step is the self-assembly to form linear aggregate due to non-uniform distribution of stabilizers on the nanoparticle surface. It was also observed that the ionic strength of the medium affects the assembly of the charged gold nanoparticles and increased assembly occurs due to increasing the concentration inorganic salt.¹⁶ The separation of metallic nanorods are very challenging due to incomplete separation or purification. This can be overcome by using surfactant which allow a relatively simple and efficient method for separation of nanorods from a mixture of rods, spheres, and platelets. Gold nanorods were separated out when cetyltrimethylammonium bromide (CTAB) surfactant was added to the concentrated dispersion of a mixture of different size rods, spheres and platelets. It was found that the larger sized nanorods were precipitated out first and then smaller sized nanorods followed by platelets. These structures are thermodynamically stable because of gaining in translational entropy compared to the orientational entropy related with nanoparticle arrangement.¹⁷ The citrate capped gold nanoparticles were assembled to form nanochains and formation of this nanochains was encouraged by the addition of CTAB surfactant. The different concentration of the surfactant leads to different architecture due to different interparticle interaction (*cf.* **Figure 5**). The suitable concentration of CTAB acts as glue that could link the (100) facets of two neighbour of gold nanoparticles. This attributed to the anisotropic distribution of the residual surface charge and generated electric dipole which are accountable for linear reorganization of gold nanoparticles into nanochains.¹⁸

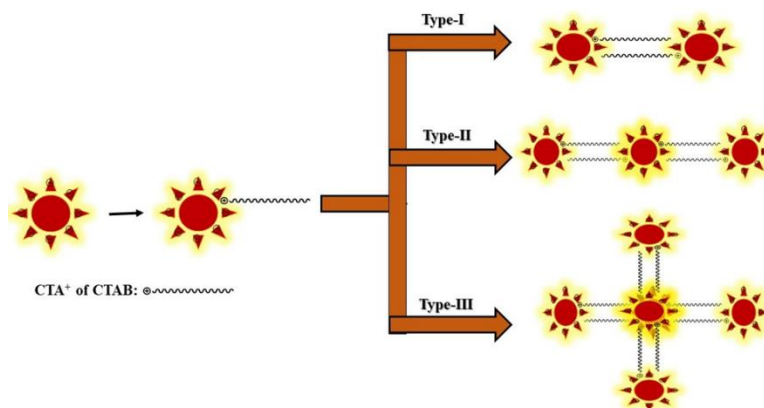


Figure 8.5: Gold nanoparticles assembly with different concentration of surfactant (CTAB).¹⁸

The non-ionic surfactant such as Tween 20, Tween 40, and Tween 60 could be guided the one-dimensional self-assembly of gold nanoparticles. The self-assembly process was controlled by the fine structure of the surfactants and proposed the non-uniform distribution of surfactant on the nanoparticle surface created the electric dipole-dipole interaction, responsible for directing the one-dimensional self-assembly process.¹⁹ The cationic surfactant CTAB molecules offer steric and electrostatic repulsion between two nanoparticle if they approach each other. The two nanoparticle can be brought together by solvent evaporation. CTAB molecules can anisotropically assisted in drawing the nanoparticle together. The rate of evaporation and concentration of surfactant would be directed different two dimensional of gold nanoparticle assembly architectures.²⁰

8.5 Application of Self-Assembly of Gold Nanoparticles:

The advancement of gold nanoparticle self-assembly synthesis promises next generation of technological applications including wearable sensors, photocatalysis, drug delivery, microelectronics, and medical diagnostics. The self-assembly of gold nanoparticle can act as acceptor due to presence of delocalized electrons and can interact with electromagnetic field of the donor dipole is the major reason for physical origin of surface energy transfer. This molecular beacon with correlation between the self-assembly of gold nanoparticle with organic dye rhodamine B and the non-radiative nano-assembly surface energy transfer can be used as spectroscopic ruler or molecular ruler in probing advanced functional materials.⁵

The coupling of surface plasmon resonance of gold nanoparticles with organic dye molecules such as rhodamine 6G can result in enriched linear and non-linear optical properties such as surface enhanced Raman scattering signal. The gold nanochains could be used as surface enhanced Raman scattering signal enhancer for rhodamine 6G.¹⁶ Gold nanoparticles in sub-nanoscale can be very easily detected by fluorescence and make them a very attractive contrast material for medical diagnostics. It was anticipated that gold nanoparticles entrapped in the unilamellar block copolymer vesicles could be utilized in the imageable drug carriers, nanoreactors or nanocarriers.²¹

8.6 Conclusions and Future Perspectives:

In conclusion, the molecules guide the nanoparticle self-assembly due to interparticle interaction involved between the nanoparticle surface ligand. These self-assembly can be chemically controlled such as pH of the solution medium, ionic strength of the solution, temperature of the mixture, as well as UV light. These self-assembly of gold nanoparticle found in various applications such as spectroscopic ruler, surface enhanced Raman spectroscopy, nanoplasmonics, biomedical, sensing, catalysis. The future of self-assembly of gold nanoparticle appears diverse and bright. The synthetic strategy for self-assembly can be improved by continuous development of experimental strategy along with the theoretical framework of the surface plasmon coupling based on the spatial configuration. The further research on gold nanoparticle assembly will give rise to novel effects, exciting discoveries, and innovative next generation of technology application specially in the organic synthesis, biomedical diagnostics, wearable sensor, photocatalysis, etc.

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9. Nanomaterials - Synthesis, Classification and Properties: Strategies Towards Sustainable Development

M. S. Shabana, C. Ragnath

Aquatic Biotechnology and Live Feed Culture Lab,
Department of Zoology,
School of life science, Bharathiar University,
Coimbatore, Tamil Nadu, India.

Dr. V. Ramasubramanian

Professor,
Department of Zoology,
Bharathiar University,
Coimbatore, Tamil Nadu, India.

9.1 Introduction:

Nanomaterials (NMs) are particles with a size of nanometers in at least one dimension. Many researchers are interested in nanomaterials because they offer unique qualities such as high physical and chemical stability, flexible chemistry for functionalization, and a large surface area. Nanomaterials on the scale of 1 to 100 nm have radically different chemical properties than materials on the micro- and macroscale. The surface area of a material grows as its size decreases. For the binding procedures, this characteristic is critical. On the nanomaterial surface, there are more binding sites. NMs are employed in a variety of fields, including biological sciences, aircraft, electronics, chemical production, and agriculture, due to their small size. Many inorganic nanoparticles are used as NMs, including carbon nanotubes, which are commonly used as carriers; iron nanoparticles, which are widely used due to their magnetism; and silica nanoparticles, which have attracted research attention due to their abundant pore structure and large specific surface area. Other research has focused on nanoparticles made of copper, gold, or silver [1]. Polymers and liposomes are organic carriers for insecticides that are renewable, biodegradable, and environmentally beneficial [2, 3]. The majority of applications for these materials are focused on increasing efficiency and productivity. They are also known as nanostructured materials (NSMs) or engineered nanomaterials (ENMs).

Nanomaterials are divided into 0D, 1D, 2D, and 3D nanomaterials based on numerous characteristics such as shape, homogeneity, dimensionality, and aggregation. These nanoparticles are used in a variety of nanotechnology applications, including the diagnosis of various diseases and the manufacturing of different processors with integrated circuits in small sizes and higher efficiency, due to their various features. As a result of this reduction, laptops are becoming lighter, cell phones are becoming smaller, and an aspect of optical fiber has replaced bundles of heavy copper wire, resulting in a technological improvement.

Because nanomaterials give increased sensitivity toward the target molecule in environmental samples and lower detection and quantification limits, they have been successfully used in a variety of environmental applications. However, significant challenges must be overcome before these nanomaterials can be commercially available in the near future. The preparation of robust, repeatable, nontoxic, biocompatible, environmentally friendly, and low-cost nanomaterials are the key challenges. Other difficulties include large-scale manufacturing and commercialization of nanomaterial-based products. We show the latest developments, problems, and industrialisation trend of NMs in many domains in this chapter.

9.2 Dimensional Structures of Nanomaterials:

A nanomaterial is a broad term that refers to all forms of nanoscale materials with unit sizes ranging from 1 to 100 nanometers. They can be found naturally or manufactured chemically, mechanically, physically, or physiologically with a variety of structures. The following is a simplified taxonomy of nanomaterials based on their structures:

9.2.1 Zero-Dimensional Nanomaterials:

All three dimensions of the materials in this category are negligibly small. Artificial atoms, often known as quantum dots, have separate energy states. Silver and gold nanoparticles are metallic nanoparticles; nevertheless, quantum dots of Cadmium selenide (CdSe) and cadmium sulphide (CdS) are included in semiconductor nanoparticles. Nanoparticles in the 150 nm range can have a variety of forms, including cubic, polygonal, and spherical.

Fullerene is one of the most well-known examples, as it is the smallest and most stable structure due to its symmetric structure. The fullerene molecule has a shape similar to that of a soccer ball. The particles are free to rotate due to weak intermolecular connections. Fullerene has the lowest surface energy due to its 0D structure [4].

9.2.2 One-Dimensional Nanomaterials:

The materials in this study have two nanometer scale dimensions, one of which is greater than the other two, implying that they have micrometer scale lengths and nanometer range diameters. Nanotubes, nanofibers, and metal or oxide whiskers, for example, are examples. They have bigger surface areas and higher aspect ratios, making them ideal for nanocomposites.

9.2.3 Two-Dimensional Nanomaterials:

These include materials having one dimension on the nanoscale scale and the other two on the micrometer scale being substantially larger than the first. 2D nanomaterials include graphene, Nano films, Nano sheets, Nano platelets, and Nano clays. Different deposition procedures are used to create thin films, which are used in a variety of fields including electronics, sensor devices, and magneto-optical devices [5]. The created Nano films have a covering or area of several square centimeters, with a thickness in the 1100 nm range.

9.2.4 Three-Dimensional Nanomaterials:

The materials in this class have three dimensions that are all outside the nanometer range. Nanocrystals or equiaxed nanoparticles are other names for these particles. All of their dimensions are greater than 100 nanometers.

Nanostructured bulk materials, also known as bulk nanomaterials, have no dimensions on the nanometer scale but are divided into equal portions on the nanometer size or contain diverse configurations of crystals on the nanoscale.

9.3 Classification of Nanomaterials Based On Chemical Composition:

Nanomaterials are classed according to their origin (natural or manmade), chemical composition (organic and inorganic), production (biogenic, geogenic, anthropogenic, and atmospheric), size, shape, and features, and research and industrial applications.

They can be categorized into many categories based on their chemical composition, such as the following:

- Metals make up the majority of metal-based materials (e.g., silver, gold, and copper nanoparticles). Metal oxide nanomaterials, such as titania, silica, and alumina, are formed of metal and oxygen.
- Nanotubes, fullerenes, graphene, and Nano spheres are carbon-based nanomaterials that include carbon in various configurations.
- Dendrimers are materials made up of highly branching macromolecules with nanoscale dimensions. Dendrimers have multiple chains on their surfaces that can be changed to perform certain activities.
- Quantum dots are auto fluorescent semiconductor nanocrystals used in in vivo biomedical imaging. They have certain unique and exciting optical properties due to their quantum confinement, such as sharp and symmetrical emission spectra, high quantum yield, distinctive chemical properties, and excellent photo stability. Binary metal complexes, such as CdSe, CdS, and CdZn, are examples.
- Nanocomposites are particular kinds of materials made by mixing two phases of distinct materials, and they tend to maintain the properties of each material employed in their development. They are classified as multiphase materials with at least one dimension in the nanoscale. Chemical properties, high thermal and mechanical stability, multifunctionality, chemical functionalization, and a large interphase zone are all features of these materials. As a result, they can be used in a variety of fields of science and technology, such as catalysis, Nano sensor and Nano probe production, sorption processes, chemical and biological applications, fuel cells, nonlinear optics, bio ceramics, high-power batteries, environmental protection, and anticorrosion agents.

9.4 Synthesis of Nanomaterials:

In general, there are two methods for making nanomaterials: (1) the bottom-up method and (2) the top-down method.

9.4.1 Bottom-Up Approaches:

The nanoparticles are first generated at the atomic level and then incorporated into the appropriate material in the bottom-up technique. Nanoparticles can be made from colloidal dispersion, and powders can be made using the sol-gel process followed by integration.

9.4.2 Top-Down Approaches:

The top-down method begins with a bulk material at the macroscopic level, which is then trimmed to the required nanoparticles. Etching and ball milling are two examples.

9.5 Characterization of Nanomaterials:

To explain the morphology of composites, crystalline phases, and average size, many techniques for characterization of nanomaterials can be used. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM), can be used to examine the composites' morphology. FTIR, Raman spectroscopy, XPS, and EDX can all be used to look for functional groups on the surface of nanotubes. The thermogravimeter (TGA) can be used to investigate thermal stability. Physisorption and chemisorption analyzers can determine the surface area, porosity, pore size, and pore distributions. By measuring the amount of gas desorbed at various temperatures, temperature programmed desorption (TPD) analyses establish the number, type, and strength of active sites available on the surface of a nanomaterial. The gas desorbs at different temperatures if there are multiple active ingredients present. The amount of reducible metal species presents in the nanomaterial and the temperature at which reduction occurs are determined via temperature programmed reduction (TPR). This can be done by determining how much analysis gas (such as hydrogen) reacts with the catalyst at various temperatures. The amount to which nanomaterials can reoxidize is determined by temperature programmed oxidation (TPO).

9.6 Properties of Nanomaterials:

9.6.1 Nanomaterials for Water Treatment:

Scientists have studied the adsorption of contaminants from aqueous solutions onto a variety of adsorbents, including activated carbons, agricultural by-products, minerals, polymers, and metal oxides. Two important properties of an efficient sorbent with high capacity and quick rate adsorption are (1) functional groups and (2) big surface area. Nanotechnology advancements present leapfrogging prospects for improving next-generation water supply systems. Nanoparticles and nanocomposites have a lot of promise for improving water and wastewater treatment efficiency and augmenting water supply through the safe use of unusual materials. Nanotechnology's extremely efficient, modular, and multifunctional processes are expected to provide high-performance, low-cost water and wastewater treatment operations that are less reliant on huge infrastructures. Nanotechnology-enabled water and wastewater treatment is projected to overcome current treatment issues and bring new treatment capabilities that could allow for the cost-effective use of unconventional water sources to extend the water supply. Adsorption, membrane processes, photocatalytic

destruction of pollutants, disinfection and microbial control, and pollutant detection and monitoring are only a few of the possibilities for nanomaterials in water treatment. The role of nanomaterials in adsorption and membrane processes-based applications will be discussed in the following sections.

9.6.2 Nanomaterials in Adsorption:

Adsorption is a technique in which a material termed an adsorbent is used to remove a soluble substance from water called an adsorbate. It is the mass transfer of adsorbate from a fluid phase to a porous surface of a solid phase via intermolecular attraction, resulting in the formation of an adsorbate film on the adsorbent surface. Nanomaterials' surface atoms are more reactive and can attract more adsorbates due to the large proportion of atoms on the surface and the increase in surface energy. Nanomaterials have a significant number of atoms with varying morphologies and the ability to act as an adsorbent for chemical species, lowering the system's free energy. Because of their: increased adsorption efficiency, greater adsorption capacity, and faster kinetics, nanomaterials offer considerable improvements in adsorption efficiency, higher adsorption capacity, and faster kinetics. Extremely high specific surface area (the nanoscale effect is attributed to a change in surface structure that creates new adsorption sites) Associated sorption sites and a larger number of surface reaction sites, such as corners, edges, and vacancies (for example, as the particle size of nanomagnetite decreased from 300 to 11 nm, its arsenic adsorption capacity increased more than 100 times [6]. Metal-based nanoadsorbents, carbon-based nanoadsorbents, and polymeric nanoadsorbents are the three types of nanomaterials used as adsorbents.

9.6.3 Nanomaterials for Pesticide Formulations:

Pesticides are critical in preventing biological disasters and increasing crop productivity. Pesticide AIs are mostly lipid-soluble [7]. NMs employed in pesticide manufacture are mostly involved in the development of nanopesticide formulation methods to improve AI bioavailability. AIs' stability is improved by NMs. Under the protection of NMs, AIs that are easily photolyzed and degraded can be stabilized. NMs can be utilized to release AIs in a targeted and controlled manner at the optimal working concentration. NMs could reduce pesticide toxicity to non-targets by taking advantage of the material's isolating effect on AIs and organisms, which is useful for expanding the pesticide's application area. Because of their antibacterial and insecticidal capabilities, NMs could be employed as nanopesticides directly. NMs have a modest size yet a large surface area effect. As carriers, NMs improve AI solubility while also protecting them from volatilization and degradation [8].

9.6.4 Nanomaterials for Fertilizer Applications:

Chemical fertilizers are currently preferred by farmers [9] because they are more effective and cost-effective than alternative fertilizers. Chemical fertilizers, on the other hand, can be overused and even squandered, resulting in soil degradation, reduced food yields, and pollution. For example, urea, which is particularly water-soluble and prone to loss, meets 80% of plant need for N-fertilizers [10]. NMs have been employed in a variety of fertilizer formulations. They're made as tunable and controllable fertilizers, and they're used to reduce fertilizer waste. These formulations improve nutrient absorption by improving soil nutrient

management, assisting in the creation of a nutrient cycle in agriculture, reducing nutrient depletion, and reducing the impact of nutrient disorder on crop output and the environment. NMs are now used as bio-fertilizers, as well as trace element fertilizers like Fe and Zn, major element fertilizers like N, P, and K, and medium element fertilizers like Si, Ca, Mg, and S. Organic fertilizer also contains NMs.

9.6.5 Nanomaterials Applications in Agrochemicals:

Many eco-friendly agrochemicals, such as bio-pesticides, have received a lot of attention in recent years as a result of the environmentally friendly control strategies advocated by Integrated Pest Management, the rapid rise of organic farming, and the increased awareness of environmental protection and food safety. NMs are then applied to these chemicals [11].

9.6.6 Nanomaterials for Bio-Pesticide Applications:

Bio-pesticides are more environmentally friendly than chemical pesticides, and they are becoming more popular for pest and disease control in plants. Bio-pesticides are now gaining market share in the following categories [12].

- Microbial pesticides
- Viral pesticides
- Plant-derived pesticides
- Biochemical pesticides

9.6.7 Nanomaterial-Mediated Nucleic Acid Pesticides System:

Because of their high specificity, low research cost, and safety, RNA pesticides are both safe and environmentally benign. As a potential environmentally benign and effective pesticide for plant protection, these insecticides fit current standards for sustainable agriculture. RNA insecticides, on the other hand, are unstable, quickly destroyed, and decay before reaching their target. NMs are used in RNAi delivery methods to preserve siRNA and increase the efficiency with which it enters bugs [13].

9.6.8 Nanomaterials Applied in Plant Growth Regulators:

NMs and PGRs are primarily used to detect trace concentrations of plant hormones in plants and to regulate hormone levels flexibly to get the best output value. NMs also aid in the absorption and transport of PGRs into plants.

9.6.9 Nanomaterials Applied in Pheromones:

Attract-and-kill through pheromones is one of the most potent approaches to integrated pest management [14], and continuous release of pheromone active substances is required during the pest capture period. However, due to the volatile nature of pheromones, their duration is usually very short, and frequent replacements are needed during field application. This is a major disadvantage of pheromones that needs to be solved. Larson et al. developed a

controlled release polyethylene dispenser for the controlled release of pheromone AIs [15]. The gel system was a three-dimensional nanoscale supramolecular network structure, providing high pheromone retention capacity.

9.7 Nanomaterials in Membrane Processes:

Membrane technology is used in a variety of separation processes, including wastewater treatment, gas separation, and desalination [16]. The selective transport of the target molecule through the membrane structure is the basis for membrane separation [17]. For the treatment of wastewater samples, Nano filtration and reverse osmosis membranes are commonly used. However, their water flux behaviour is hampered by a thick separating layer. Nanomaterials (graphene, fullerenes, carbon nanotubes, and nanoparticles) can be incorporated into the membrane structure to offset this disadvantage. The combination of membranes with nanoparticles that have great physical and chemical properties gives outstanding physical and chemical stability, as well as high rejection of the target substance to be isolated from the sample.

9.7.1 Carbon Nanomaterial-Based Membranes:

Carbon nanoparticles are widely used in the construction of innovative nanocomposite membranes because they offer unique properties such as excellent mechanical, chemical, and thermal stabilities, large surface area, superior optical properties, and decreased density. Nanocomposite membranes are frequently developed by incorporating carbon nanomaterials such as graphene, carbon nanotubes, and fullerenes into the membrane structure [18]. The integration of nanoparticles with membranes not only provides excellent physical and chemical stability, as well as high rejection and flux behaviours, but also introduces diverse traits such as catalytic and antibacterial properties to the produced nanocomposite membranes [19].

9.7.2 Graphene-Based Membranes:

Graphene was discovered by Geim and Novoselov in 2004 [20]. Since then, so much efforts were put into the design and development of new graphene-based functional materials. Owing to the excellent hydrophobic feature of graphene, it was widely used in the preparation of functional materials with superhydrophobic features. Recently, these superhydrophobic functional materials were efficiently applied for the separation of water oil mixture [21].

9.7.3 Carbon Nanotubes-Based Membranes:

Many researchers have concentrated on the usage of CNTs in various applications since their discovery in 1991 [22]. Carbon nanotubes (CNTs) are cylindrical structures made up of coiled graphene sheets that are classified as MWCNTs or single-walled carbon nanotubes. CNTs have a number of advantages, including great oleophobicity and hydrophilicity [23], as well as outstanding mechanical, electrical, and thermal properties [24, 25]. The design and preparation of innovative nanocomposite membranes can be successfully carried out by combining these unique properties with membrane systems.

9.7.4 Fullerene-Based Membranes:

Fullerenes are a type of carbon allotrope with 60 carbon atoms arranged in hexagons and pentagons. The form of fullerenes and carbon nanotubes is the primary distinction. In the nanoscale, fullerenes are cage-like structures, whereas CNTs are tube-like structures [26,27]. Fullerenes were utilized as effective nanomaterials in membrane architectures, and the fullerene-based nanocomposite membranes generated were successfully used to remediate environmental samples such as wastewater. Chen and colleagues, for example, created a nanocomposite membrane made of polyvinyl butyral/polyvinylidene fluoride and fullerene covered with F-127 [28].

9.7.5 Nanoparticle-Based Membranes:

Nanoparticle-based membranes are another prominent material for separation operations. Yu et al., for example, developed a polysulfone membrane based on yttrium nanoparticles and modified with polyvinyl alcohol for the effective separation of arsenate from water [29]. Gold nanoparticle-based polydopamine (pDA)-polyethyleneimine nanocomposite membranes for the efficient removal of salts from water samples were produced in another fascinating study [30]. The generated gold nanoparticle-based composite membranes also demonstrated outstanding antibacterial efficacy against *Escherichia coli* and *Staphylococcus aureus*, according to the findings. The production of polyethylene nanocomposite membranes with silica nanoparticles for humic acid removal from water samples was described by Akbari and colleagues [31].

9.7.6 Molecularly Imprinted Polymer-Based Membranes:

MIPs are custom-made materials with specialized binding sites for the molecule of interest [32]. MIPs are made by polymerizing appropriate functional monomers with a cross-linker and the desired molecule, often known as a "template". Designing and constructing new membranes with excellent selectivity and penetration behaviour toward the target compound/s remains a critical and difficult task. Recent research has shown that combining membrane technology and molecular imprinting technology to build composite membranes is an excellent strategy. These composite membranes can be used to effectively separate target molecules [33].

9.7.7 Metal Nanoparticles:

Metal nanoparticles [such as silver (Ag) and gold (Au) nanoparticles] are promising materials as efficient adsorbents in environmental analysis because they have excellent features such as very small dimensions and large surface area to volume ratios, which ensure excellent adsorption capacities for target compounds in environmental samples.

Silver nanoparticles, for example, are effective materials with excellent antibacterial properties due to their very toxic effects on various microorganisms such as viruses and bacteria. As a result, Ag NPs have been effectively used to identify and separate microorganisms from contaminated environmental samples such as water.

Due to their ease of synthesis with reducing agents such as hydroxyl amine and citrate, gold nanoparticles (Au NPs) are also efficient nanomaterials similar to Ag NPs. To improve their binding efficacy toward the target chemical, Au NPs can be implanted into various adsorbents.

9.7.8 Biomimetic Materials:

Biomimetic materials are created by creating artificial duplicates of biomaterials found in nature. These biomaterials are utilized in tissue culture, cell development, biotechnological manufacturing, and other applications where the original materials have failed to perform their roles or are used to maintain the environment. Several peptides and proteins are made using biomimetic materials, which are created or have designs borrowed from nature. A variety of polymers have been developed to improve mechanical characteristics and strength [34]. The first stage in a biomimetic method is to discover the performance of biomaterials found in natural systems, and then to figure out how they work, which can be done using scanning probe microscopy.

9.8 Conclusion:

This chapter provides a comprehensive summary of nanomaterials' recent progress in several domains. The rapid growth of nanomaterials has opened up new possibilities for the design and fabrication of innovative nanomaterials in environmental sciences, such as Nano sensors, Nano sorbents, Nano tools, and portable Nano devices. To avoid unwanted repercussions on natural ecosystems, safety assessments of artificial nanomaterials in systems other than no target, including biological systems, should be closely investigated. Studies of their destiny and behaviour in natural environmental settings, such as soil and water, would aid in the management of nanomaterials with potential toxicological implications. It is envisaged that successful examples of nanomaterials-based products in the environmental sciences will be commercially available in the future, thanks to the efforts of researchers from various departments of study such as chemistry, medicine, pharmacy, biology, and material science engineering.

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10. Nano-Technology and Its Relevance in Higher Education

Shalini

Assistant Professor,
Department of Teacher Education,
Vivek College of Education,
Bijnor.

Prerna Verma

Assistant Professor,
Department of Home Science,
Vivek College of Education,
Bijnor.

Abstract:

This paper outlines about the Nanotechnology and its need and importance in higher education and examines how will work Nanomaterial's in modern era or in future. Significant paper exists relating to the question of whether Nanotechnology or Nanotechnology bared product merit special government regulation this paper is related to the circumstances in which it is necessary and appreciate to assess new substances prior to their release into market, community and environment.

This technology can be the combination of science and engineering involved in the design, synthesis, and uses of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale. At these scales, consideration of individual molecules and interacting groups of molecules in relation to the bulk macroscopic properties of the material or device becomes important, hence it is control over the basic molecular structure that allows control over the macroscopic chemical and physical properties.

Applications to medicine and physiology imply materials and devices designed to interact with the body at molecular scales with a high degree of specificity. This can potentially translate into targeted cellular and tissue-specific medical applications designed to get maximum therapeutic affects with minimum side effects. In this article the main scientific and technical aspects of nanotechnology are introduced and some of its significant clinical applications are discussed.

Keywords:

Manipulation of matter, Nanomaterial, Nanoscale, Molecular Nanotechnology, Bottom up approaches and top - down approaches. Nanocomposites, nanocataysts.

10.1 Introduction:

At atomic and molecular scale, there is the manipulation of matter in Nano technology. Generally, it works with materials, devices and other structures with at least one dimension sized from 1 to 100 nanometers with a variety of potential application, neonate is a key technology for the future and government have invested billions of dollars in its research. It is very diverse, ranging from extension of conventional device physics to completely new approaches bared upon molecular self-assembly, from developing new materials with dimension on the Nano scale to direct control of matter on the atomic scale.

Nanotechnology implicates the application of fields of science as diverse as surface science, chemistry, molecular biology, semiconductor physics, micro fabrication etc. It may be able to create new materials and devices with a vast range of applications, such as in medicines, electronics, biomaterials and energy production. On the other hand, Nanotechnology varies many of the same issues as any new technology including concerns about the toxicity and environmental impact effects on the global economics, as well as speculation about various doomsday sceneries.

K. Eric Drexler developed the concept of Nanotechnology and founded the field of molecular Nanotechnology. The coming era of Nanotechnology, which proposed idea of “Nanoscale assembles” which would be able to build a copy of itself and of other items of arbitrary complexity Drexler’s vision of Nanotechnology is after called “Molecular Nanotechnology.

Government moved to promote & found research into Nanotechnology with programs such as the national Nanotechnology initiative. The early 2000 also saw the beginnings of commercial application of Nanotechnology although there were limited to bulk application of Nonmaterial. Such as the silver Nano platform for using silver Nan particles as an antibacterial agent, Nonparties- based transparent sunscreens, and carbon Nanotubes for stain resistant textiles.

In the original sense, Nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete higher performance product.

10.2 Approaches Used in Nanotechnology:

Two main approaches are used in Nanotechnology:

1. Bottom-up approaches
2. Top-down approaches

10.2.1 Bottom-Up Approaches:

In the “Bottom-up” approach, materials and device are built from molecular components which assemble themselves chemically by principles of molecular recognition.

DNA Nanotechnology utilizes the specificity of Watson- crick base pairing to construct well defined structures out of DNA and nucleic-acids.

Approaches from the field of classical chemical synthesis (inorganic and organic synthesis) also aim at designing molecules with well-defined shape. (eg- bis- peptides).

There is a scanning probe lithography technique where an atomic force microscope (AFM) tip is used patterns directly on a range of substances with a variety of inks.

10.2.2 Top-Down Approaches:

In the “top-down” approach involves the breaking down of bulk materials in Nano sized structures or particles. Top down synthesis technique are extension of those that have been used for producing micron sized particles.

A material such as gold (chemically inert) can serve as a potent chemical catalyst at Nanoscale much of the fascination with Nanotechnology stems from these quantum and surface phenomena that matter exhibits at the Nano scale.

Many technologies that descended from conventional solid state silicon methods for fabricating microprocessors are now capable of creating features smaller than 100nm, falling under the definition of Nanotechnology.

Nanoelectromechanical system (NEMSs) is devices that constitute electrical and mechanical functions at the Nanoscale. It consists of miniature electrical and mechanical apparatuses such as beams, sensors, pumps, resonators and motors etc.

Focused ion beams can directly remove material or even deposit material when suitable precursor gasses are supplied at the same time.

10.3 Nanomaterials:

The Nanomaterials field includes subfields which study materials having specific properties arising from their Nanoscale dimension.

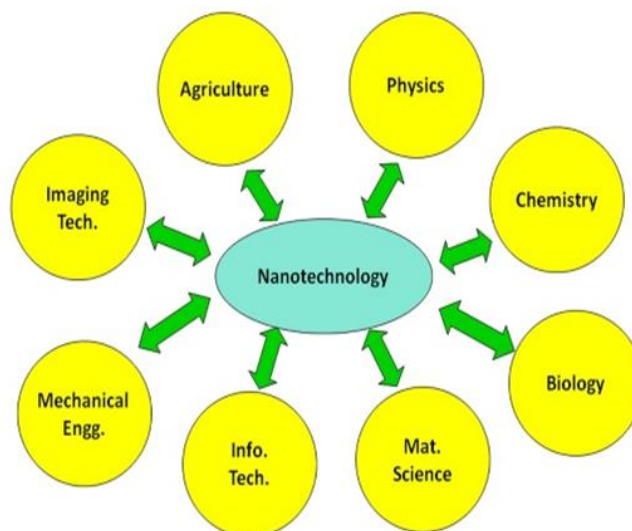
- Interface and colloid science has given rise to many materials which may be useful in Nanotechnology and other fullerenes, and various Nanoparticles and Nanorods Nanomaterials with fast ion transport are related also to Nanoinionics and Nanoelectronics.
- Nanoscale materials can also be used for bulk application most present commercial applications of Nanotechnology are of these flavors.
- Progress has been made in using these materials for medical application.
- Nanoscale materials are sometimes used in solar cells which combats the cost of traditional silicon solar cells.
- Development of application incorporating semiconductor Nanoparticles to be used in the next generation of product such as display technology lighting solar cells and biological.

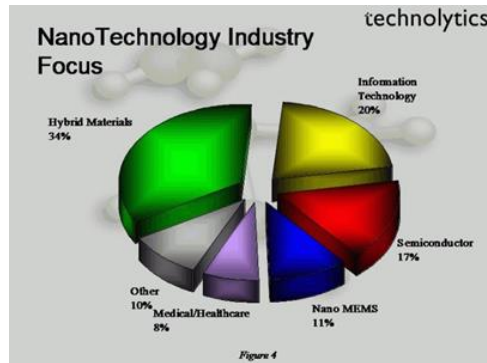
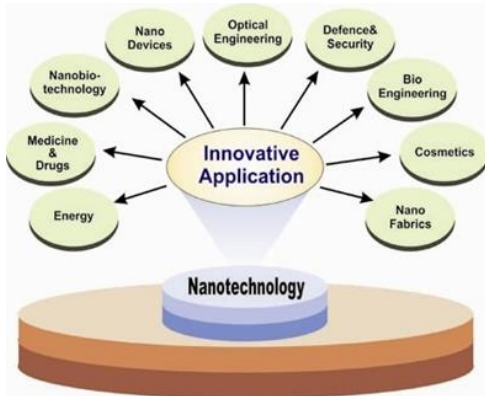
10.4 Application:

One of the major applications of Nanotechnology is in the area of Nano electronics with MOSFET'S is being made of small Nanowires ~ 10nm in length.

The 2000S has seen the beginning the application of Nanotechnology in commercial products, although most application are limited to the bulk use of passive Nanomaterials eg- include titanium dioxide and zinc oxide Nanoparticles in sunscreen, cosmetics and some food product. Silver Nonparties in food packaging clothing application such as silver Nano carbon Nanotubes for stain resistant textiles and cerium oxide as a fuel catalyst.

- a. Nano medicine
- b. Green Nanotechnology
- c. Energy applications of Nanotechnology
- d. Industrial application of Nanotechnology
- e. Potential application of carbon Nanotubes.
- f. Group improvement
- g. Nano biotechnology
- h. Analysis of gane expression and regulation
- i. Soil management
- j. Plant disease diagnostics
- k. Water management
- l. Precision agriculture
- m. Bioprocersing
- n. Post-harvest technology.



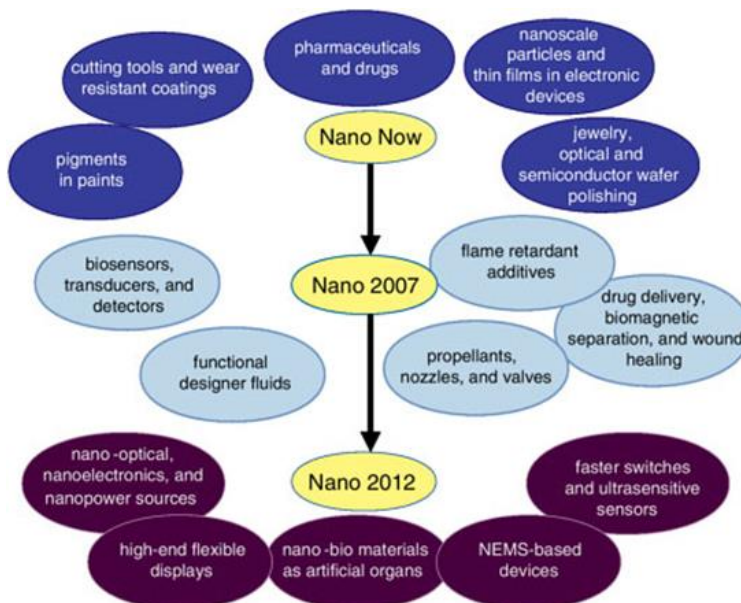


10.5 Nanotechnology in Present:

Today, Nanotechnology is among the fastest growing areas of science and technology with exponential progress being made. The first integrated circuits using three dimensional carbon Nanotubes these could be vital in maintain the growth of computer power, allowing Moore’s law to continue Solar panels with greater effacing through the use of Nanomaterials composites.

Nano structured polymers in display technologies allowing brighter images lighter weight less power consumption and wider viewing angles. Nanotechnology surface which are highly resistance to bacteria dirt and scratches. New fabrics that are highly resistance of liquid caring it to simply fall off without Leaving any dampness or stains. Nano structured catalysts used to make chemical manufacturing processes more efficient saving energy reducing waste products.

Some Examples of How Nanotechnology Impacts Our Lives Now:



10.5.1 Nano Composites:

Researchers have developed a coating process to make sponge-like silica latch onto toxic metals in water. Self-Assembled Monolayer's on Mesoporous Supports simply captures such metals as lead and mercury, that area unit then recovered for reprocess or contained in place forever. PNNL One is an example of a SAMMS nanocomposite (Self-Assembled Monolayer's on Mesoporous supports) An hexagonally close-packed cluster of tubular pores (end view) is shown in the foreground. A single pore, during this case coated with a mercaptopropylsiloxo, is shown with in the background.

- **Impact:**

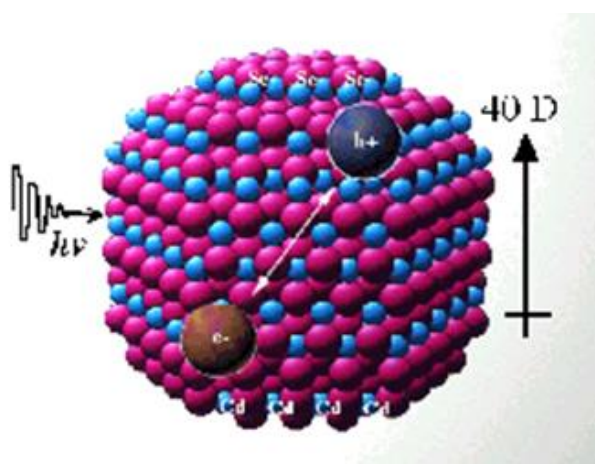
Will likely be used on other GM and Toyota models soon, and in other areas of their vehicles, as well as the other auto manufactures, lowering weight, increasing mileage, and creating longer-lasting autos. Likely to impact repair shops (fewer repairs needed) and auto insurance companies (fewer claims). Except National Aeronautics and Space Administration, the ESA, and different space-faring organizations to require a significant look, soon, which is able to eventually lead to lower raise prices, which is able to lead to additional material being upraised into area.



- **Nanocrystals:**

Nanocrystals of many metals have been shown to be 100 percent, 200 percent and even as much as 300 percent rigid than the same materials in bulk form. Because wear resistance often is dictated by the rigidness of a metal, parts made from nanocrystals might last significantly longer than conventional parts. The nanocrystalline coating of silver fastly kills a broad spectrum of bacteria in as little as 30 minutes. "In photovoltaic devices, Nano crystals are the perfect light harvester. They absorb sunlight more strongly than dye

molecules or bulk semiconductor material; therefore, high optical densities can be attained while maintaining the requirement of thin films. Perfectly crystalline CdSe nanocrystals are also an artificial reaction center, separating the electron hole pair on a femto second timescale. Fluorescent nanocrystals have several benefits over organic dye molecules as fluorescent markers in biology. They are incredibly bright and do not deteriorate. Drug-coupled nanocrystals attach to the protein in an extracellular fashion, enabling movies of protein trafficking. They also form the basis of a high-throughput fluorescence assay for drug discovery."



10.5.2 Nanoparticles:

Sunscreens are utilizing nanoparticles that are extremely effective at absorbing light, especially in the ultra-violet (UV) range. Due to the size of particle, they unfurl more easily, cover better, and save money since you use less. And they are transparent, unlike traditional screens of white color. These sunscreens are so successful that by 2001 they had captured 60% of the Australian sunscreen market.

- **Impact:**

sunscreen maker has to convert to using nanoparticles. And other product manufactures, like packaging makers, will find ways to assimilate them into packages to decrease UV exposure and successive spoilage. The \$480B packaging and \$300B plastics industries will be directly consummated.

By the use of aluminum nanoparticles, Argonide has created rocket propellants that burn at double rate. They also produce copper nanoparticles that are incorporated into automotive lubricant or the reduction of engine wear.

AngstroMedica has produced a Nano particulate-based synthetic bone. "Human bone is made of a calcium and phosphate combindly called Hydroxyapatite. By manipulation at molecular level of calcium and phosphate, we have created a patented material that is similar in structure and composition to natural bone. This synthetic bone can be used in the treatment of fractures and soft tissue injuries."

10.5.3 Nanostructured Materials:

OLED color screens (made of nanostructure polymer films) which is produced by Kodak used in car stereos and Mobiles. OLEDs (organic light emitting diodes) may enable lighter, more flexible, thinner, less power consuming displays, and other consumer products such as cameras, PDAs, laptops, televisions, and other as yet undreamt of applications.

10.5.4 Nanotubes:

Nanoledge (a company) makes carbon Nanotubes. Carbon Nanotubes are frequently used for commercial purpose such as mundane (marketing tactic) use is in a tennis racket. The yoke of the racket bends less by the effect of ball. As a result, the performance of players is improved.

- **Impact:**

Once companies like Nanoledge can ramp up their production from grams, to pounds, to tons, then world becomes their oyster: everywhere strength and weight are a factor - such as in the aerospace, automobile, and airplane industries - they will make a major impact.

10.5.5 Nano catalysts:

All nanoparticles have been used from the outset in the manufacture of automotive catalytic converters: The surface area of the particles increases perilously as the particle size decreases and the weight remains the same. Many chemical reactions only take place on the surface of the catalyst. The area of surface and activity of catalysts are positively correlated. As larger the surface area, the more active the catalyst. Thus Nanoscale catalysts are the boon for many chemical process because by the use of Nano scale catalysts, the rate of chemical reaction increases effectively.

Shenmue Group (china's largest company) has licensed technology from Hydrocarbon Technologies that will enable to liquefy coal and turn it into gas. In this process a gel-based Nanoscale catalysts are used, which increases the efficiency and reduces the cost.

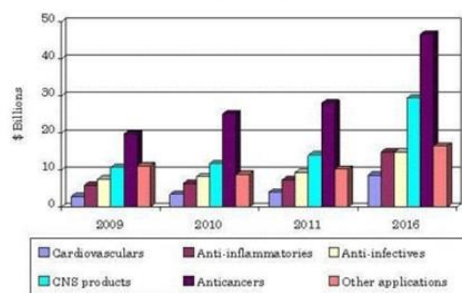
- **Impact:**

"If the technology keeps up its promise and can economically convert coal into gasoline, diesel and fuel. Then coal-rich countries such as the U.S., China and Germany could depend meagerly on imported oil. At the same time, acid-rain pollution would be less because the liquefaction strips coal of harmful Sulphur."

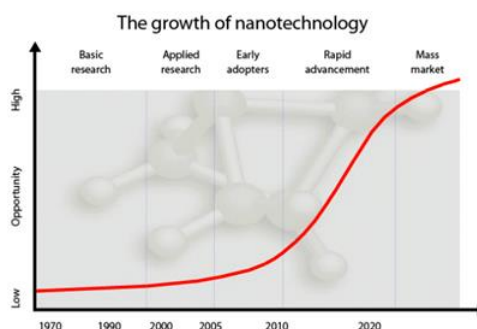
10.6 Nanotechnology in Present:

By 2025 Nanotechnology is expected to be a mature industry with countless mainstream products graph.

SUMMARY FIGURE
NANOMEDICAL GLOBAL SALES BY THERAPEUTIC AREA, 2009-2016
(\$ BILLIONS)



Source: BCC Research



The possibilities seem ceaseless. In the field of Nano electronics and computer technology, nanotechnology will permit the construction of smaller circuits and computers. Smaller circuits will run faster which are responsible for greater computer speeds. Computers will have a much longer life due to new Nano materials. A laptop computer could therefore have its efficiency increased by millions living longer and working faster to give far better value for money.

Nanotechnology has significant impact on the environment and environmental energy. solar cell can become more efficient if we use Nano sized solar cells as they provide much of the energy needed around the world. It also increases the efficiency of the fuel cell and batteries. In the future, nanotechnology will be used to tackle environment problems. New green processing technology can be adapted to minimize the generation of undesirable by products.

In health care and medicinal biology, the Nano -sensors are being developed in the next 5 years and they will be used for fast and accurate diagnostics. Further ahead, nanotechnology will be used to build artificial muscle and 'lab on a chip' technology will develop more efficient drug discovery processes.

There are many other future applications of nanotechnology and more possibilities will come to light as it is developed more. Nanotechnology offers major opportunities for the UK economy and it is key by which any country can make its base excellence in science and technology. Critics of nanotechnology insist that a strict regulatory system should be introduced to ensure risks are minimized and it is the responsibility of government to ensure that procedures are seriously adapted or not. if not then proper action should be taken by government.

Further in the future Nanotechnology will play a major role in medicine and longevity blood cell sized devices will go directly into human body, eradicating pathogens virtual reality and many other advanced treatments will become possible through the use of "Nanorods".

In more distant future, Nanotechnology could allow humans to make the transition to fully non- biological forms. At atomic scale, entire body and brain could be reconstructed which leads to practical immortality.

10.7 Nanotechnology and Higher Education:

The Nanotechnology undergraduate education (NUE) in engineering program aims at introducing Nanoscale science engineering and technology through a variety of interdisciplinary approach into undergraduate engineering education. The focus of the program or Nanoscale engineering education with relevance to devices and systems and on the societal ethical and economic or environmental issues relevant to Nanotechnology.

The EMM- Nano program is truly integrated with a strong research backbone and on important international scope. The objective of the programme is to provide a top quality multidisciplinary education in Nano- Science & Nanotechnology.

The national institute for occupational safety and health has conducted initial research on how Nanoparticles interact with body's system and how workers might be exposed to Nano sized particles in the manufacturing or industrial use of Nanomaterials. The most instant challenge in nanotechnology is that we need to know more about materials and their properties at the nanoscale. Universities and corporations across the world are strictly studying how atoms combined together to form larger structures.

Education and training in nanotechnology is supported by the Commission through a system of Research Training Networks. New hybrid technologies, combining nanotechnologies, materials sciences, engineering, information technologies, biotechnology and environmental science, are developing those days.

This evolution requires such multidisciplinary networks over a wide range of research areas, as well as strong collaboration across traditional scientific borders between Nanotechnology researchers inside the European Union and worldwide.

- **Potential Risks:**

It can broadly be grouped into four areas-

- a. Health issues
- b. Environmental issues
- c. Societal issues
- d. Speculative issues

10.8 Conclusion:

Nanotechnologies may provide new solution for the millions of people in developing countries who lack access to basic services such as safe water, reliable energy, health care and education. The united nations have set millennium development goods for meeting these needs potential opportunities of Nanotechnologies to help address critical international development priorities include improved water purification system, energy system, medicine and pharmaceuticals, food production and nutrition and information and communication technology and all this will possible only when Nano science will become a part of higher education.

So that all student could know about Nanoparticles or Nanomaterials and show should start many program in the field of Nano Science in higher education that aims to enhance the quality of higher education in Nano science in order to promote India as a center of exallence in learning around the world.

As a result of nanotechnology Humanity will be faced with a powerful, accelerated social revolutions. In the future, a team of scientists will succeed in constructing the first Nano-sized robot which will be capable of self-replication. Consumer goods will become abundant, affordable, smart, and long lasting. Medicine will take a quantum leap forward. Travelling in space and colonization will become safe and economical. For these and other reasons global lifestyles will change radically and human behaviour drastically impacted.

This powerful combination of materials science and biotechnology will create entirely new processes and industries and put India among the world leaders thus leads to a Nano technological revolution. As the paper unveils the commercial application of nanotechnology, the consumer may appreciate the potential behind it. The decision of the consumer whether to accept it or reject it remains vital to the future of Nan technological industry and in pace with the world economy. Hence a clear perceptive will give clarity to the consumers to make the right decision in terms of accepting what technology that Nano offers.

- **Chemistry:**

Education in chemistry provides support for all teacher of chemistry across the secondary further and higher education sectors it aims to strength the community by providing high quality peer reviewed content tools and resources which promote the shearing of best practice and innovating teaching.

Chemistry education (or chemical education) is a comprehensive tern refers to the study of the teaching and learning of chemistry in all school. College and university. Topic in chemistry education might include understanding how student learn chemistry how best to teach chemistry and how to improve learning outcomes by changing teaching method and appropriate training of chemistry teacher, within many modes including classroom lecture demonstrations and laboratory activities. There is a constant need to update the skills of teacher engaged in teaching chemistry, and so chemistry education spears to this need.

- **Philosophical Prospective (How to Work in Chemistry):**

There are at least 4 different philosophical prospect-ive that describe how the work in Chemistry education is carried out. The first is what one might call a practitioner's perspective, where in the individuals who are responsible for teaching chemistry (teacher, instructor, professors) are ones who ultimately define chemistry education by their action.

A second prospective is define by a self-identify group of chemical educations, faculty members and instructors who, as opposed to declaring their pre interest in a typical area of laboratory research (organic, inorganic, bio- chemistry)

A third prospective is chemical education research (CER) tends to take the theories and method developed in pre-college. Science education research which generally take place in school of education and applies them to understanding comparable problems in post-secondary setting.

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11. An Overview of Nanotechnology (Materials and Applications)

Prof. Tanmay Ghosh

Department of Microbiology,
Dinabandhu Andrews College,
Kolkata, W.B., India.

Abstract:

Nanotechnology is gaining prominence rapidly as a highly potent technology. Its immense potential promises the possibility of significant changes in near term future, once the most essential machines - called the Universal Assembler and the Nano computer are built.

Today the products manufactured employing nanomaterials having general as well as unique applications like curing cancer, phosgene detection, energy harvesting for self-powered Nano systems, chip manufacturing, batteries, aerospace materials etc. The research in the area of carbon nanotubes, nano-polymers, nano-vectors, nanocomposites, nanocrystals, nanoparticles, nanofibers, nanoclays, nanotubes, nanofilters, nanohorn, nanowires, Nano springs, Nano rods etc. have been reported. Particles smaller than 100 nm are typically associated with nanotechnology, as are nanomaterials made from nanoparticles.

Nanotechnology is also being developed for use in drug delivery, biosensors, and other biomedical applications. Further, nanotechnologies are also being developed for use in environmental applications, e.g., clean-up of environmental pollutants.

Keywords:

Nanoscale, Quantum Size Effect, Nanotechnology, Nanometers, Molecule.

11.1 Introduction:

At atomic, molecular, or macromolecular levels in the range of approximately 1-100 nanometers to provide fundamental understanding of phenomena and materials at the nanoscale. [1] A nanometer is a millionth of a meter in length. The diameter of a human hair is around 10,000 nanometers. Because of their minuscule size, nanoscale structures, devices, and systems are a primary application of nanotechnology.

He coined the phrase "nanotechnology" in a paper he wrote in the 1970s. It's technically correct to say that the term "Nanotechnology" refers to an area of applied science and technology concerned with manipulating matter at the atomic and molecular level, which is typically at or below the size of 100 nanometers. [2]

Approaches used in nanotechnology

- **Bottom-Up Approach:**

The "bottom-up" approach uses molecular components to build materials and devices, which assemble chemically through molecular recognition principles. To put it another way, the goal of this type of assembly is to combine tiny parts into larger ones.

- **Top-Down Approach:**

When using the "top-down" technique, nano-objects are built from larger things without atomic-level control. Smaller devices are assembled by using larger ones as a guide for their construction. [3]

11.2 Applications of Nanotechnology:

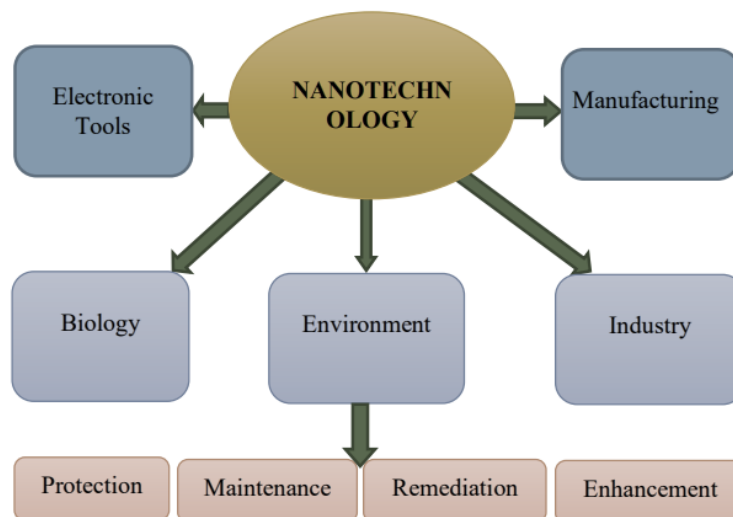


Figure 11.1: Applications of Nanotechnology

- **Medicine and Drug Delivery:**

With medical nanotechnology, treatment would be more accurate and efficient. A minuscule Nano tool could save a patient from a gruesome and dangerous surgical procedure by preventing the need to open up their entire body. Precision in medical treatment is possible with nanotechnology, which eliminates the need for medicine prescription that is based on trial and error. A comprehensive picture of the body's systems and activities, including the underlying cause of disease and potential treatments, may be automatically gleaned from a single laboratory test using high-tech computers. [4] Medical malpractice would be eradicated and the adverse effects of taking drugs based on doctors' guesses would be avoided if nanotechnology was used in medicine. Detection and prevention of diseases can be easily accomplished with modern medical technology. As long as diseases can be averted, human longevity and quality of life will both improve?

- **Energy Sector:**

This technology opens the door to the creation of smaller, more efficient, and more effective energy-producing, absorbing, and storing systems. Batteries, solar cells, and fuel cells, for example, can all be made more compact while maintaining their functionality.

- **Development of Quantum Computer:**

Nanotechnology can actually revolutionized a lot of electronic products as nano transistors, nano diodes, quantum computers etc. and their procedures and applications. Quantum computers are groups of billions of customized atoms that are created and manipulated using nanotechnology.

Quantum computers represent data differently than any classic computer. [5] While a classical computer represents data in bits that either “0” or “1”, a quantum computer uses quantum bits to represent “0’s,” “1’s,” and both “0’s” and “1’s” simultaneously. Because quantum bits can represent both 1’s and 0’s at the same time it is possible to do many calculations simultaneously.

- **Reactivity and Strength of Materials:**

As a result of their high surface area to volume ratio, nanoparticles are far more reactive than larger particles. It's been discovered that iron nanoparticles can remove pollutants from groundwater more effectively than other media. It's possible to make bulletproof vests out of carbon nanotubes because they're exceedingly robust. [6]

- **Food Nanotechnology:**

In the food industry, nanotechnology has opened up a wide range of new possibilities. Food packaging and preservation are two areas that have recently acquired popularity in this field. Prognoses of substantial economic advantages in this area have helped to draw attention to it. According to data, sales of nanotechnology products for food and beverage packaging will top \$20.4 billion in the United States by the year 2010. Carbon nanotubes are one of the most promising nanomaterials in this field.

The same tube may have antimicrobial effects in addition to improving the mechanical properties of food packaging materials. Nanomaterials may also be useful in the preservation of food. When food spoilage microorganisms come into contact with Nano sensors that fluoresce in a variety of colors, they could provide a solution. Food poisoning cases could be reduced as a result, as the detection time would be shortened.

Food packaging is already using Nano silica and Nano selenium, which is said to enhance selenium absorption in a beverage. [7] Although it can also be used to purify water, nano-iron is more commonly used as a health supplement. Nanosalt, which is still in the early stages of development, has to be mentioned for its ability to reduce salt intake in the diet.

11.2.1 Nanomaterials:

Materials with morphological characteristics smaller than one tenth of a micrometer in at least one dimension are known as nanomaterials. For example, nanomaterials have unique physical and electrochemical properties that allow for the creation of stronger, tougher, and more wear-resistant products. Carbon nanotubes, different fullerenes, various nanoparticles, and Nano rods are only a few of the materials that interface and colloid research has produced. In nanotechnology research, members of the fullerene family are a key focus. [8]

11.2.2 Review of Literature:

Nanotechnology is enhancing the efficiency of fuel generation from normal and low-grade raw petroleum materials through better catalysis, as well as fuel consumption efficiency in automobiles and power plants through higher-efficiency combustion and less friction (Low et al., 2015) [9]. Nano-bioengineering of enzymes is trying to enable conversion of cellulose into ethanol for fuel, using wood chips, maize stalks (not just the kernels, as today), and unfertilized perennial grasses (Chaturvedi and Dave, 2014) [10]

Nanotechnology is enhancing the efficiency of fuel generation from standard and low-grade raw petroleum materials through better catalysis, as well as the efficiency of fuel consumption in automobiles and power plants through higher-efficiency combustion and reduced friction (Low et al., 2015).

The nano-bioengineering of enzymes is aimed at making it possible to turn wood chips, corn stalks, and unfertilized perennial grass into ethanol for fuel. [9] (Chaturvedi and Dave, 2014) [11] Impurities in water can be detected quickly and inexpensively using nanotechnology, which can then be filtered and purified at a minimal cost (Rabbani et al., 2016[12]; Sobolev and Shah, 2015[13]; Mishra et al., 2012[14]).

The building industry will gain greatly from nanotechnology in the future. Self-cleaning windows and concrete capable of devouring pollution are just two examples of how this new technology may transform building materials into new levels of energy, light, strength, security and beauty (Halicioglu, 2009). [15]

Nanomaterials like carbon nanotubes and carbon Nano horns are also being used in energy applications because of their potential to provide outstanding conductivity for charge transportation (Yimin, 2011) [16]. PbTe-based quantum dot superlattice system, for example, has shown an increase in energy conversion. In order to create more energy-efficient thermoelectric devices, it has been proposed that this feature be reproduced (Yimin, 2011). [16]

11.2.3 Objectives:

- To investigate the use of non-technological methods
- To learn more about the food delivery system and nanotech.
- Researching nanotechnology's meaning

- To learn more about nanotechnology's techniques.

11.3 Research Methodology:

It is the systematic, theoretical investigation of the methods used in a particular field of research. Theoretical analysis of a branch of knowledge's methodologies and principles is included.

Parameters like paradigm, theoretical model and phases are typically included in this type of research. In this study, many studies on learning and research linked to the issues are analysed and reviewed in detail.

Journals were gathered from internet databases that primarily focus on journals for their subject matter and content. This topic's identification centre on the study's materials, participants, and methods of instruction.

Classification accuracy and items, methods, and results were the primary criteria for identifying research publications. Using the findings of the analysis, a systematic overview of the learning and research in the themes was developed.

11.3.1 Result and Discussion:

E. coli and other pathogens can be rapidly, sensitively, reliably, and simply isolated and detected using nanotechnology.

Quantum dots, localized surface plasmon resonance of metallic nanoparticles, improved fluorescence, dye immobilized nanoparticles, and metallic nanoparticles immobilized with a Raman reporter molecule are a few of the nanotechnology-enabled detection approaches. [17]

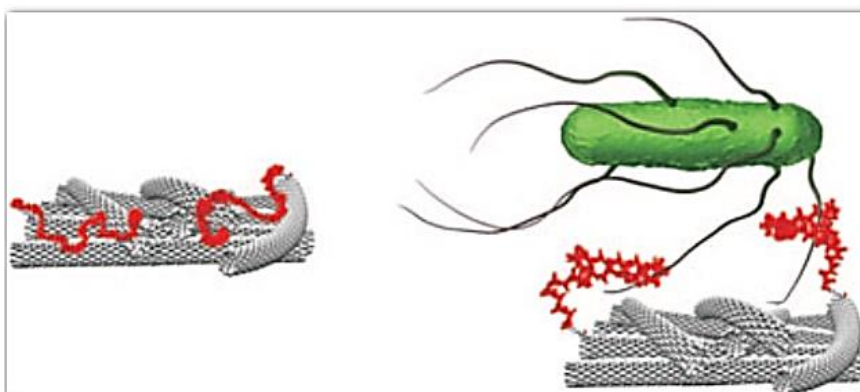


Figure 11.2: Detection of Foodborne Illnesses

The promise of "personalized medicine" can be realized if successful medication development is achieved through the use of such therapies and diagnostics in clinical

practice. [18] For diagnostics and therapies, Figure 11.3 shows how the two markets have grown and how they will grow in the future.

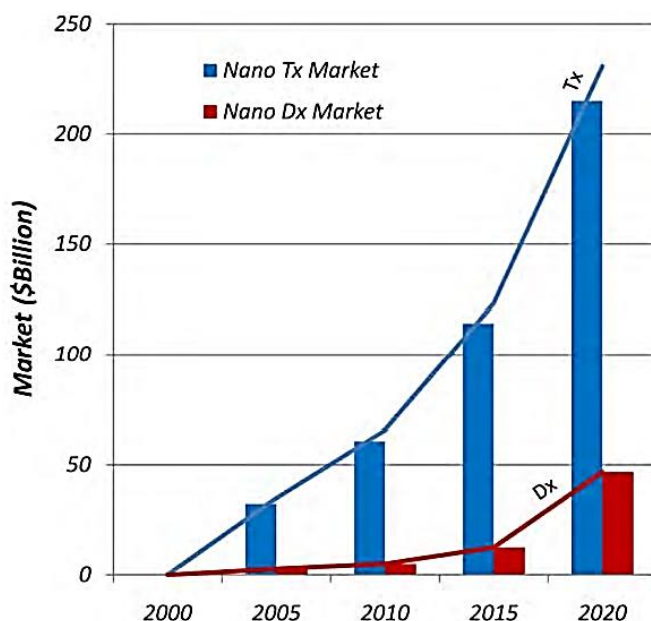


Figure 11.3: Historical and Projected Markets for Nano Therapeutics (Tx) and Nano Diagnostics (Dx).

Current food and agricultural nanotechnology research, includes processing, packaging, nano-additives, cleaning, and pollutants sensors, and future advancements in the burgeoning field of agri-food nanotechnology. [19]

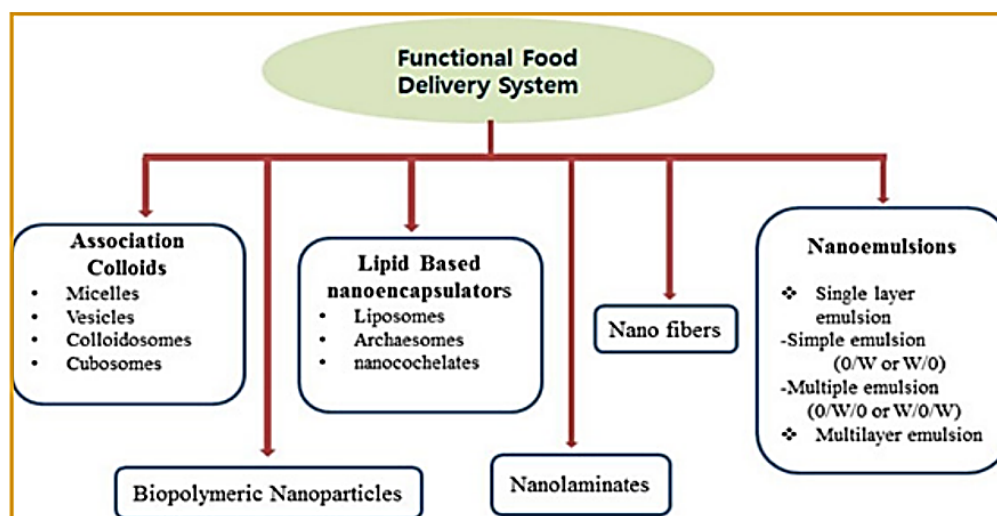


Figure 11.4: Food Delivery System

Nanotechnology may also have the ability to improve the quality and safety of food products. Nano sensors are being tested for their potential to detect pathogens in food systems in a number of research. Materials made with nanotechnology, or goods grown, processed, or packed with the help of nanotechnology, are referred to as nonfoods. [20]

11.4 Conclusion:

When it comes to food and agriculture, construction materials, mechanical, medical, and electrical engineering, nanotechnology has the potential to open the door to a new world. However, despite the fact that replicating natural systems holds great promise, scientists are still grappling with their astounding complexity.

Manufacturing, energy, environmental science, information and communication technology (ICT), and medical research could all be transformed by nanotechnology. When considering nanotechnology as one of numerous developing technologies, it is important to keep an eye out for the temptations of research hype.

Concerns about immediate dangers and assessments of the broader impact of such technologies on human nature and human futures, both in their individual and global dimensions, must also be given careful study. When evaluating these new technologies, it is necessary to look beyond the specific risks and benefits associated with each application and ask more general questions in order to identify and fill any conceptual gaps that may arise in such a quickly growing area of research and development.

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12. Characterization Techniques

Dr. Padmakar G. Chavan

Assistant Professor,
Department of Physics,
Kavayitri Bahinabai Chaudhari North Maharashtra University,
Jalgaon, Maharashtra.

Abstract:

Characterization of materials is the basic and important aspect of nanotechnology. Various extra ordinary properties can be explored deeply by characterization techniques. The nanomaterials possess various features in terms of surface morphology, optical properties, chemical properties, mechanical properties etc.

These all properties are further studied in detail with the help of characterization techniques. Hence, this chapter gives emphasis on X- ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM). Photoluminescence (PL).

Keywords:

Nanomaterials, Characterization, Nanotechnology.

12.1 Introduction:

Nanomaterials are known to be prominent for various applications due to their extraordinary properties. Various Characterization techniques came forward for the detail investigation of these Nanomaterials, Which involves X-ray diffraction (XRD), Scanning electron microscope (SEM), Transmission Electron Microscopy (TEM), Photoluminescence (PL), etc.

These techniques are popular for identification of crystal structure, size, surface topography, purity and elemental composition etc. The Characterization techniques plays important role in the field of nanotechnology and material science.

12.2 X-Ray Diffraction (XRD):

Crystallographic structure and physical properties of materials can be reveal by XRD which is non-destructive technique which are in the form of powders and thin films. Wavelength of X-rays is of the order of an angstrom ($\text{\AA} = 10^{-10} \text{ m}$), which is falls in the range of inter planer distances.

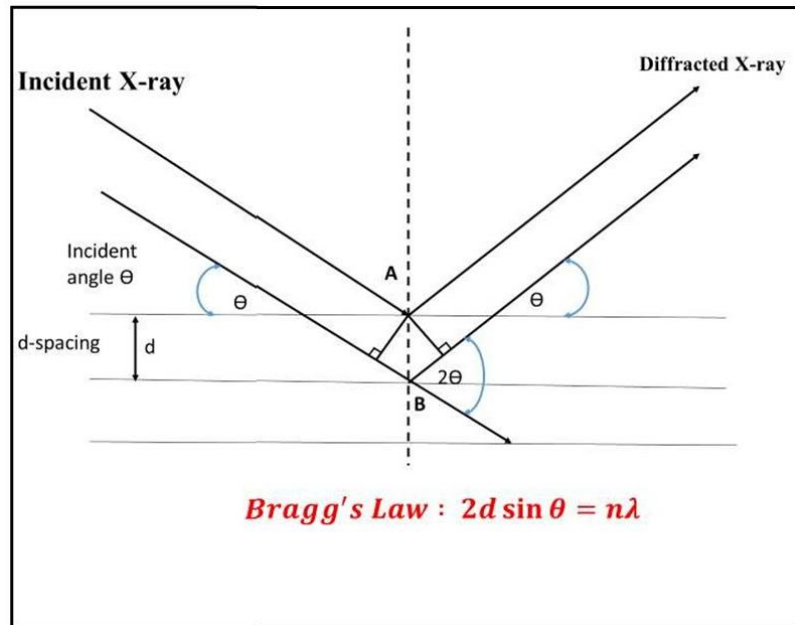


Figure 12.1: Schematic of X- Ray Diffraction Process

Hence, crystalline materials give response to X-rays and constructive diffraction pattern forms. Collective information is presented in the form of diffracted peaks of uneven intensities.

Bragg's law is necessary condition for X-ray diffraction,

$$2d\sin\theta = n\lambda \quad (1)$$

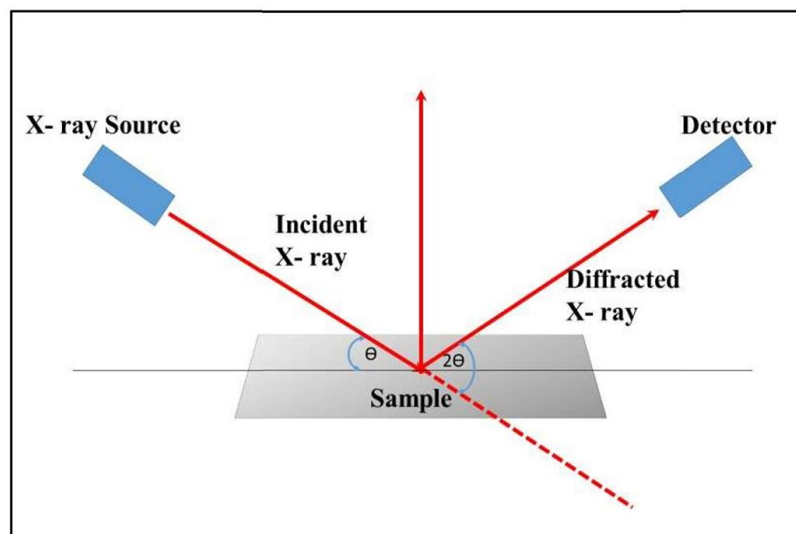


Figure 12.2: Schematic of X-Ray Diffraction Set-Up

The information such as type of crystal structure as well as inter atomic spacing associated to crystal can be withdrawn from XRD pattern. XRD is most popular for high accuracy and also it is absolute technique.

12.3 Scanning Electron Microscope (SEM):

In case of nanometric film the surface topography plays an important role. The information of surface topography can be directly achieved by SEM. Out of all possible interaction secondary electron is responsible for the image formation in SEM. The electron beam is scanned over the specimen. The SEM is useful for organic and inorganic specimens. In addition to surface topographic information SEM has additional facility of elemental mapping, which is useful for identification of various element.

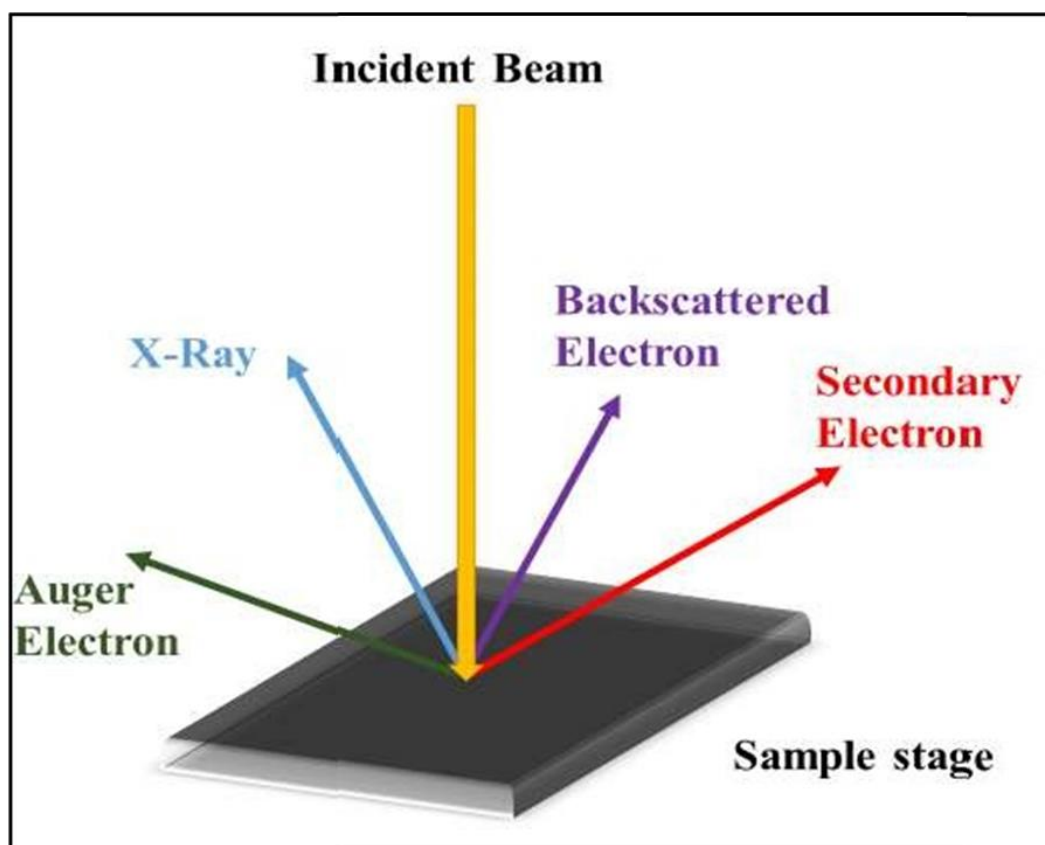


Figure 12.3: Schematic of Electron Interaction Processes

When primary electrons interact with specimen, various processes take place out of all secondary electron's emission is quite important. The amplification of output signal is further carried out for the formation of clear and high-resolution image. Elemental mapping is quite important when we doped some element is host material. By analysing the energy associated to high energy electrons, elemental mapping is possible. All elements one can be detect in the elemental mapping except few.

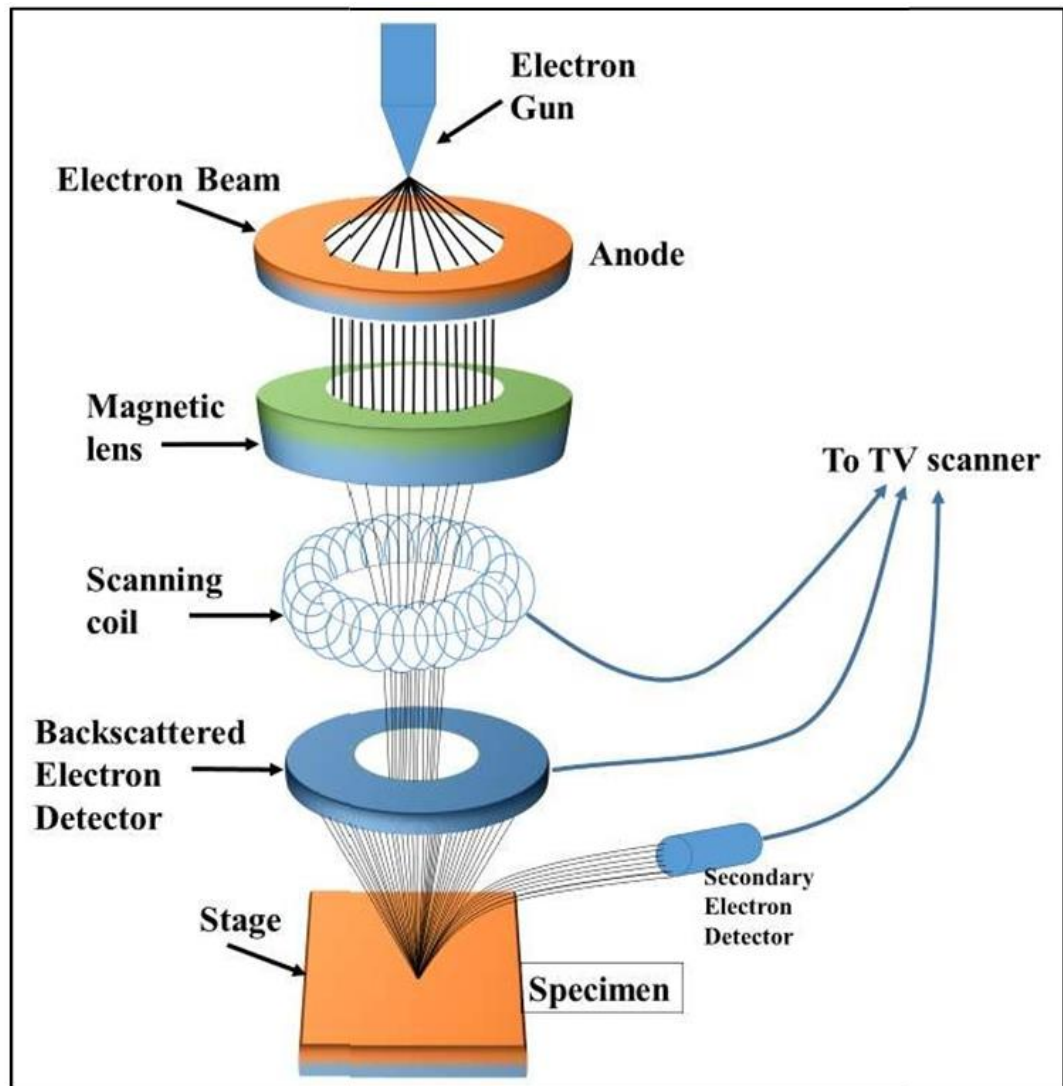


Figure 12.4: Schematic of Scanning Electron Microscopy (SEM) Technique

12.4 Transmission Electron Microscope (TEM):

The crystal structure, inter atomic spacing and defect in the crystalline materials can be obtained by one of the powerful techniques such as (TEM). In addition, to physical properties of nanomaterials their crystal structures are also quite important which has most of hidden information.

Such information can be explored by TEM technique. Further, defects and crystallographic planes can be viewed by High resolution TEM (HRTEM) technique. Constructive interference pattern is the Key parameter for TEM [1].

High vacuum is minimum requirement of TEM. Voltage range of 40-200 kV is capable to accelerate the electron which are coming out from thermionic gun. The maximum thickness of the order of 0.1–0.3 μm for corresponding 100 keV is required [2]. Like optical microscope TEM has facility of various lenses. Because of these electromagnetic lenses coherent and parallel beam of electron is produced. The feature which defines angular range of electron is the aperture. The process of clear TEM image is depends combinations of lenses used.

12.4.1 Bright Field Imaging:

Elastic and inelastic scattering are responsible for change in energy spread as well as angular range. Stopping of unnecessarily scattered electron is done by aperture kept in the back focal plane (Figure. 12.5). Bright field image is captured in the absence of image if the aperture is placed at optical axis [1]. Dark portion will appear in image due to high thickness and high density of material/specimen.

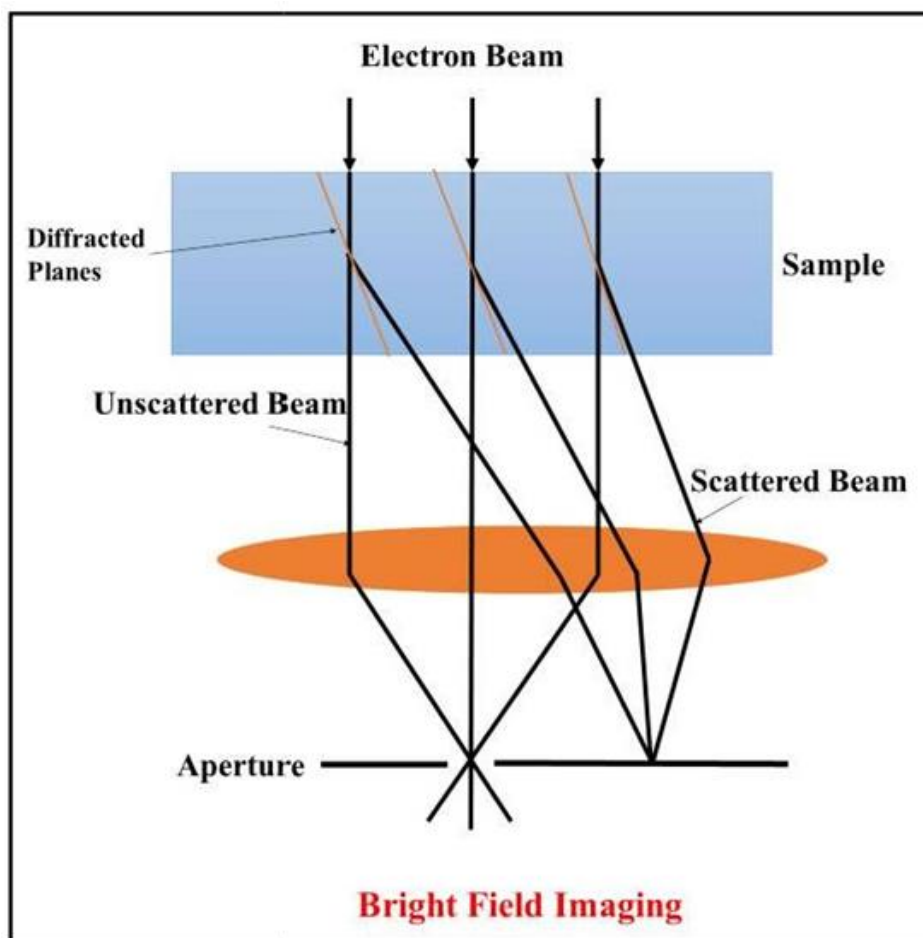


Figure 12.5: Bright Field Imaging Schematic View

12.4.2 Dark Field Imaging:

In case of dark field imaging aperture can be used for particular selection of diffracted beam. The TEM is known for generation of information in reciprocal space as well as in real space [1].

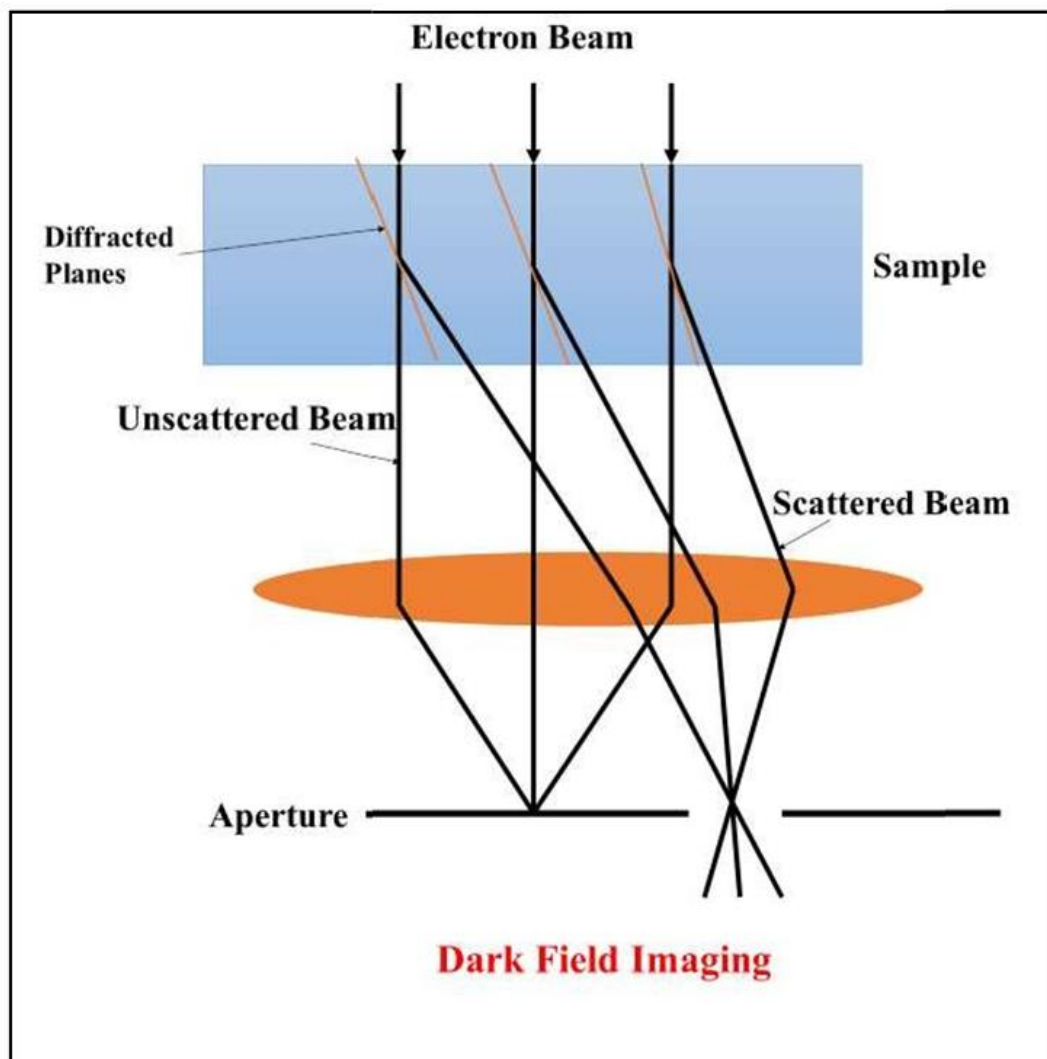


Figure 12.6: Dark Field Imaging Schematic View

12.5 Photoluminescence (PL):

As the various defects and impurity occurred in the nanometric film, the detection of such defects is quite important. PL spectroscopy has capability to withdraw above said information. The PL is known for non contact and non-destructive technique.

In typical process light beam interact with specimen and various processes take place (Figure 12.7). Upon the absorption of light electron excitation and recombination is takes place through various processes, as given below and also in Figure 12.7

- a. Electron hole pair generation,
- b. Recombination through defects states,
- c. Recombination through band to band,
- d. Emission of hole

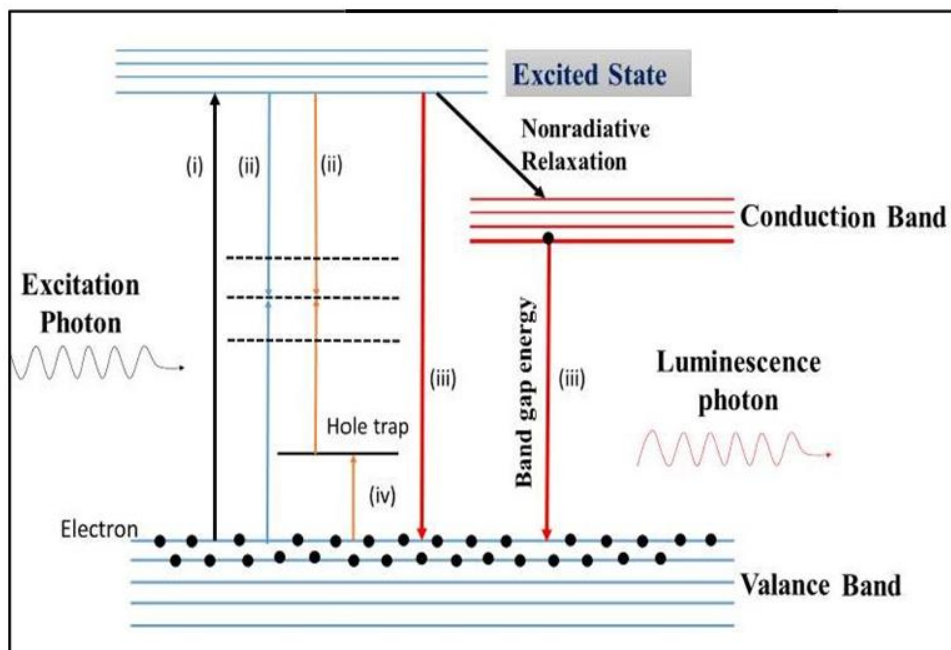


Figure 12.7: Schematic of Various Interactions in Photoluminescence Spectroscopy [3]

If the recombination follows laws of radiatively then one can identify defect or impurity in state. In this process energy levels lies near to conduction or valence band are dominantly take participation. Core levels are known for non-radiative recombination.

In detailed experimentation, Xenon (Xe) arc lamp is usually used. The wavelength range of Xe lamp is 300 to 1100 nm. A filter is usually used for the wavelength selection which further relates with the analysis of specimen.

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13. Synthesis of Nanoparticles for Various Applications

G.V.S. Subbaroy Sarma

Department of Humanities & Sciences,
Malla Reddy Engineering College Campus 1,
Dulapally Road, Maisammaguda Post via. Kompally,
Rangareddy Dt. Secunderabad,
Hyderabad, Telangana, India.

M. Jemimah Carmichael

Department of Civil Engineering,
Vignan's Lara Institute of Technology and Science,
Guntur, Andhra Pradesh, India.

Murthy Chavali

Office of the Dean (Research) & Division of Chemistry,
Department of Science, Faculty of Science & Technology,
Alliance University, Chandapura-Anekal Main Road,
Bengaluru, Karnataka, India.

Abstract:

Nanotechnology refers to the creation and utilization of materials whose constituents exist at the nanoscale; and, by convention, be up to 100 nm in size. Nanotechnology explores electrical, optical, and magnetic activity as well as structural behaviour at the molecular and sub-molecular levels. The synthesis of nanoparticles is an active area of academic and, more significantly, applied research in nanotechnology. Materials scientists and engineers have made significant developments in the improvement of methods of synthesis of nanomaterials. In this chapter, various methods of preparing nanomaterials including chemical methods like Chemical reduction method, Microemulsion/colloidal method, Sono chemical method, Electrochemical method, Solvo thermal decomposition, and Physical methods like Pulse laser ablation, Mechanical/High ball milling method, ball milling method, Mechanical chemical synthesis, Pulsed wire discharge method are discussed in detail. The distinctive properties of nanomaterials make them uniquely suitable for such a wide range of functions. Due to its wide applications in electronics, coatings, optical materials, and catalysis the alloy, and nanomaterials are of tremendous interest nowadays.

The increased use of nanoparticles in biomedical sciences, electronics, and drug delivery has led to the development of various methods of synthesizing nanoparticles using physical, chemical and biological methods. However, limitations like toxicity, hazardous chemicals and high cost of production led to the development of alternative methods for

the production of nanoparticles. Green synthesis of nanoparticles is an alternative and emerging area of research. The green synthesis of nanoparticles using microorganisms is a promising approach, which is an ecofriendly and cost-effective method.

Keywords:

Nanotechnology, nanoparticles, Physical methods, Chemical methods, Green synthesis, applications.

13.1 Introduction:

Nanotechnology is an emerging field of science. The base of nanotechnology is nanoparticles. The size of nanoparticles ranges from 1 to 100 nm. One nanometer is one billionth of a meter (10^{-9}). Therefore, nano-science and nanotechnologies deal with at least clusters of atoms of 1nm size. Nano-science is the study of materials that exhibit remarkable properties, functionality and phenomena due to the influence of small dimensions. Today's nanotechnology harnesses current progress in chemistry, physics, material science, biotechnology and electronics to create novel materials that have unique properties because their structures are determined on the nanometer scale. Some of these materials have already found their way into consumer products, such as sunscreens and stain-resistant plants. Nanotechnology is an excellent example of emerging technology, offering engineered nanomaterials with great potential for producing products with substantially improved performances. Nanotechnology is the construction and utilization of functional structures designed from atomic/molecular scale and with at least one of its characteristic dimensions in nanometers [1]. Such materials and systems can be rationally designed to exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of their size. Phenomena at the nanometer scale are likely to be a completely new world. Properties of matter at the nano-scale may not be predictable from those observed at larger scales [2]. Important changes in behaviour are caused not only by continuous modification of characteristics with diminishing size but also by the emergence of totally new phenomena such as quantum confinement, a typical example is the colour of the light emitting from semiconductor nanoparticles depending on their sizes[3]. Designed and controlled fabrication and integration of nano-materials and nanodevices is likely to be revolutionary for science and technology. Nanotechnology can provide unprecedented understanding of materials and devices, and is likely to influence many fields.

13.2 Classification of Nanoparticles:

The nanoparticles are classified into different types based on morphology, size and shape. Some of the important classes of nanoparticles to mention are,

13.2.1 Organic Nanoparticles:

The organic nanoparticles include ferritin, micelles, dendrimers and liposomes shown in Figure 13.1. The organic nanoparticles are not toxic, and biodegradable and some organic nanoparticles have a hollow sphere i.e. micelles and Liposomes. It is also familiar with the name of nanocapsules, which are heat and light-sensitive [4]. Organic nanoparticles are an

ideal choice for drug delivery due to these characteristics. Then nanoparticles are also widely used in target drug delivery. The organic nanoparticles are also known as polymeric nanoparticles. The most known shape of organic or polymeric nanoparticles is nanosphere or nanocapsule [5].

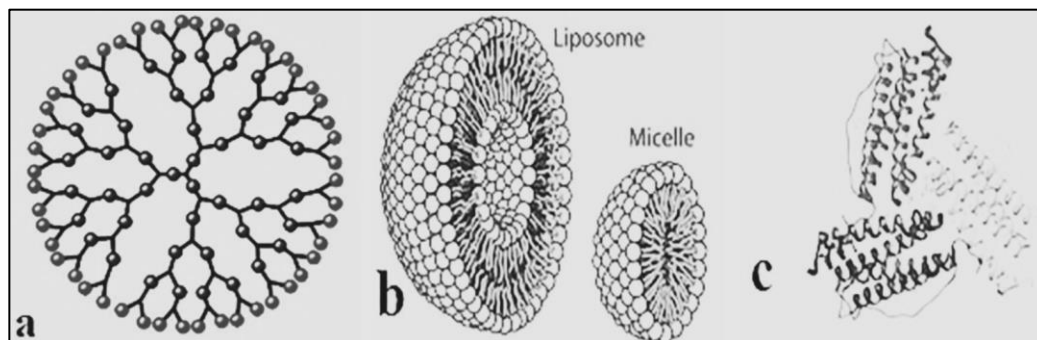


Figure 13.1: Organic nanoparticles (a) Dendrimers (b) Liposomes and Micelles (c) Ferritin

13.2.2 Inorganic Nanoparticles:

Carbon is not present in inorganic nanoparticles. The inorganic nanoparticles are not toxic. The inorganic nanoparticles are biocompatible and hydrophilic. The inorganic nanoparticles are highly stable than organic. The inorganic nanoparticles are classified into metal and metal oxide nanoparticles.

A. Metal Nanoparticles: Metals are used to synthesize Metallica nanoparticles by using destructive or constructive methods. The metal precursors are used to make the pure metal nanoparticles. The metal nanoparticles possess unique optoelectrical properties due to plasma on resonance characteristics. The synthesis of metal nanoparticles is controlled by shape, facet and size [6]. The nanoparticles of all metals can be synthesized [7]. The nanoparticles of aluminium, gold, iron, lead, silver, cobalt, zinc, cadmium and copper are well-known metal nanoparticles.

B. Metal Oxide Nanoparticles: The purpose of the synthesis of metal oxide nanoparticles is to modify the property of their respective metal nanoparticles such as iron nanoparticles being oxidized to iron oxide nanoparticles. The reactivity of iron oxide nanoparticles is increased as compared to iron nanoparticles. Due to an increase in reactivity and efficiency of metal oxide, the nanoparticles of metal oxides are synthesized [8]. Examples of metal oxide nanoparticles are zinc oxide, silicon dioxide, iron oxide, aluminium oxide, cerium oxide, titanium oxide and magnetite.

C. Ceramic Nanoparticles: Ceramic nanoparticles are also known as nonmetallic solid. The ceramics nanoparticles are synthesized via heating or successive cooling. The ceramic nanoparticles may be polycrystalline, amorphous, porous, dens or hollow form [9]. The researcher focuses on these nanoparticles due to their wide application such as photodegradation of dye, photocatalysis, catalysis and imaging applications [10].

D. Bio Nanoparticles: Bio-nanoparticles is an assembly of atom or molecules that is prepared in the biological system having at least one dimension in the range of 1–100 nm. All bio nanoparticles are naturally occurring nanoparticles. These nanoparticles are divided into two categories intracellular structure and extracellular structure. Magnetosomes are an example of intracellular structure and lipoproteins and viruses are examples of extracellular structure. Magnetosomes, exosomes, ferritin, lipoproteins and viruses are examples of bio nanoparticles.

13.3 Classification of Nanomaterials:

Nanomaterial is such material, which has a structural component or unit less than one micrometre in at least one dimension. Building blocks of matter are considered nanomaterial.

13.3.1 Carbon-Based Nanomaterial:

The carbon-based nanomaterials are completely composed of carbon [11]. Fullerenes, carbon nanotubes, graphene, carbon black and carbon nanofibers are the classes of carbon-based nanoparticles.

A. Fullerene:

The fullerenes may be C₆₀ or C₇₀ shown in Figure 13.2. The fullerenes consist of nanomaterials in the form of a hollow cage. Due to their electrical conductivity, electron affinity, structure, strength and versatility, it becomes a noteworthy commercial interest [12]. Fullerenes consist of carbon units in the form of pentagonal and hexagonal shapes. The carbon atoms in fullerenes are linked to each other by sp² hybridized. The fullerenes are made of C₆₀ or C₇₀ having diameters of 7.114 and 7.648 nm. The fullerene may be a single layer or multilayer.

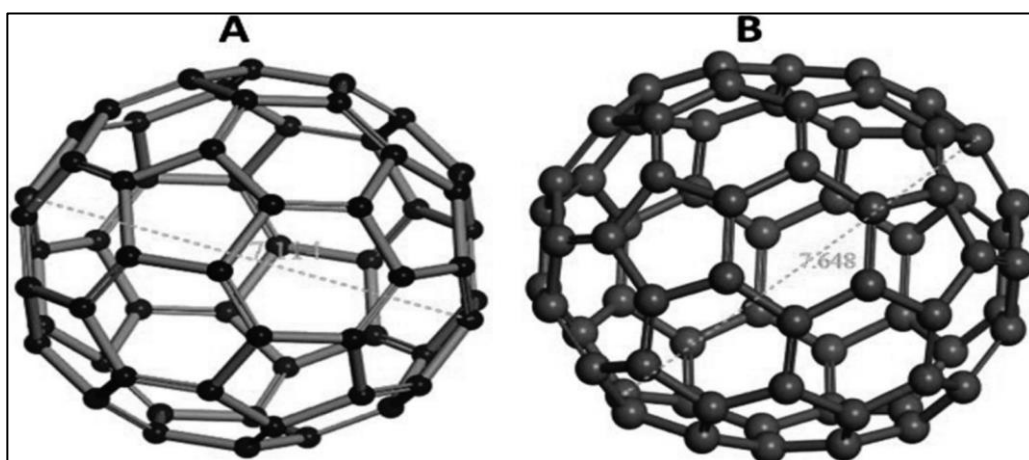


Figure 13.2: Different forms of Fullerenes (A) C₆₀ and (B) C₇₀

B. Carbon Nanotubes (CNT):

Carbon Nano Tubes are tubular elongated structures having 1–2 nm diameter [13]. The carbon nanotube can be predicted as semiconducting or Metallica based on diameter [14]. The structure of CNT resembles with graphite sheet rolling upon itself. Based on rolling CNT categorize into single-walled (SWNTs), double-walled (DWNTs) and multi-walled (MWNTs) as shown in Figure 13.3.

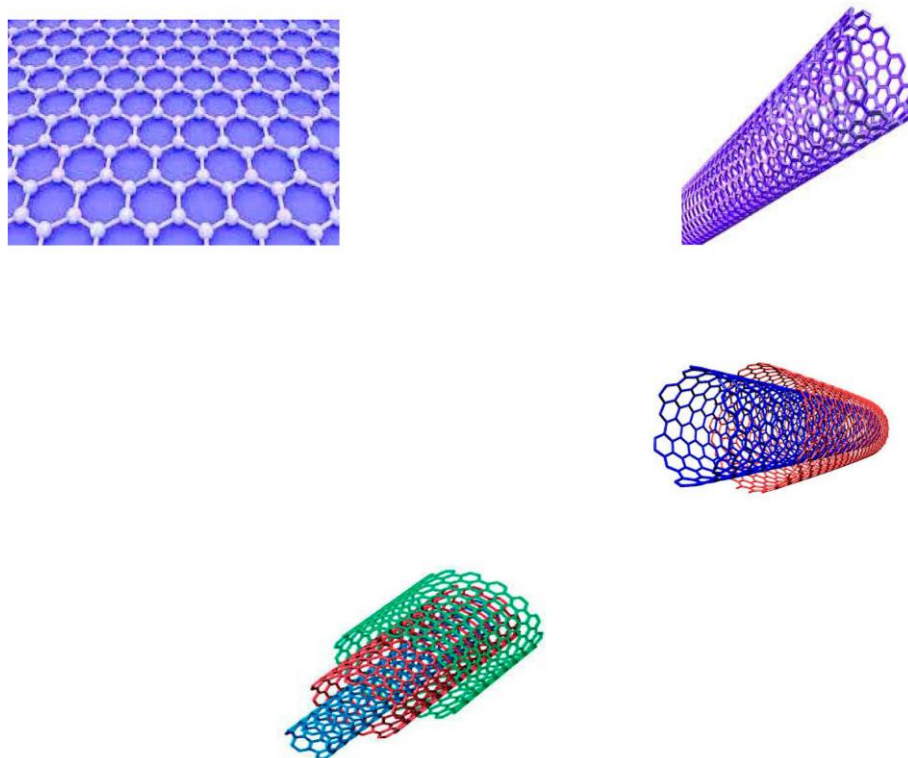


Figure 13.3: Types of CNT

a. Single-walled carbon nanotubes (SWTs). - Single-walled Nanotubes (SWTs) consist of single rolled sheets. The least diameter of nanotubes for single-walled is 0.7 nm.

b. Double-walled carbon nanotubes (DWNTs). - Double Walled Nanotubes (DWNTs) consist of double-rolled sheets.

c. Multi-walled carbon nanotubes (MWNTs). - Multi-walled Nanotubes (MWNTs) consist of multiple rolled sheets. The Nano foil of graphene having honeycomb carbon lattice is wound into a hollow cylinder to form nanotubes. The length of carbon tubes ranges from a few micrometres to several millimetres. CNT is strong, it can be easily bent and regain its original shape without brittle when released [15]. CNT shows various structures and shapes, different thicknesses, lengths and number of layers but the characteristics of CNT are based on sheets of graphene [16].

D. Graphene:

A graphene is an allotropic form of carbon. It is a hexagonal network of honeycomb carbon atom lattices having a two-dimensional planar surface. The graphene is 1 nm in thickness.

E. Carbon Nanofiber:

The nano foil of the same graphene is transferred into carbon nanofiber as carbon nanotubes but nano foils are wound into cups or cones instead of elongated cylindrical tubes.

F. Carbon Black:

It is an amorphous material which is made up of carbon. The shape of carbon black is spherical. The diameter ranges from 20 to 70 nm. High interaction between the particles is present and so bound in an aggregate shown in Figure 13.4.

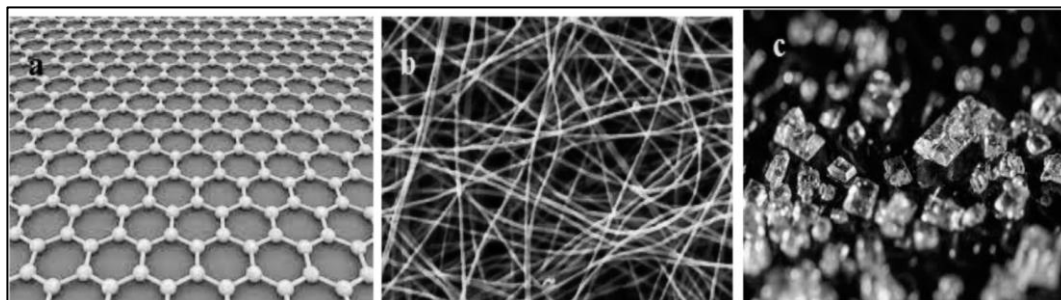


Figure 13.4: (a) Graphene sheet (b) Carbon nanofiber (c) Carbon black.

13.4 Synthesis of Nanoparticles:

The synthesis of NPs can be carried out following two different approaches, viz., (i) top-down approach, and (ii) bottom-up approach as shown in Figure 13.5. Furthermore, three different strategies such as physical, chemical, and biological methods are adopted for the synthesis of NPs.

Top-down approach: In this method, the suitable starting material is reduced in size using physical or chemical means. Several methods including the commonly used attrition and pyrolysis can be used for the physical synthesis of metallic nanoparticles. In attrition, macroscale or microscale particles are ground by a size-reducing mechanism.

Bottom-up approach: It refers to the construction of a structure atom-by-atom, molecule-by-molecule, or cluster-by-cluster. In this approach, initially, the nanostructures' building blocks are formed and, subsequently, assembled into the final material using chemical or biological procedure(s) for synthesis.

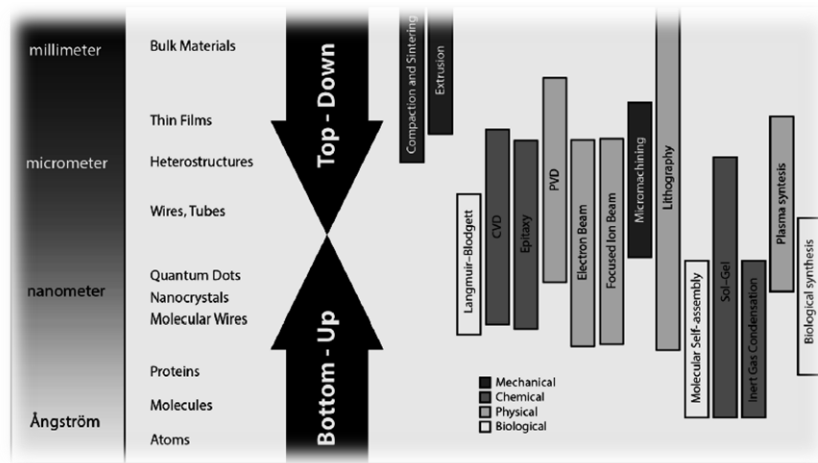


Figure 13.5: Schematic Representation of Building Nanostructures

A part to direct atom manipulation, there are various widely known methods for producing nanomaterials: physical, chemical, and mechanical

13.4.1 Physical Methods:

A. Physical Vapour Deposition:

This technique involves the use of materials of interest as sources of evaporation, an inert gas or reactive gas for collisions with material vapour, a cold finger on which clusters or nanoparticles can condense, a scraper to scrape the nanoparticles and a piston-anvil. All the processes are carried out in a vacuum chamber so that the desired purity of the end product can be obtained. Figure 13.6 schematically illustrates a set-up for carrying out physical vapour deposition and compressing the powder in a pellet form.

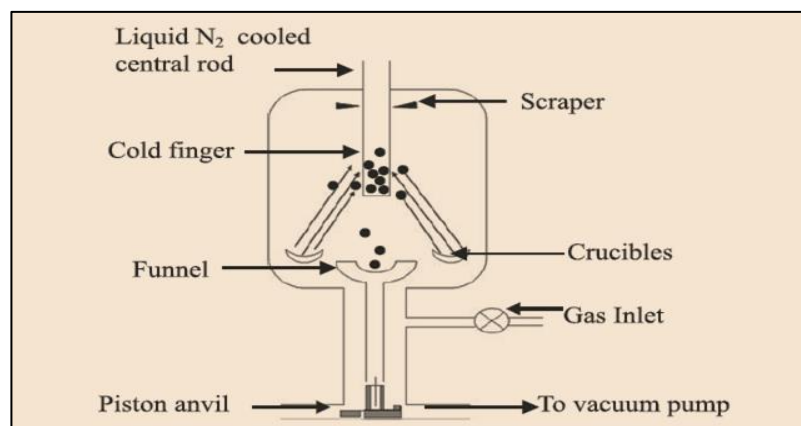


Figure 13.6. Schematic diagram of the synthesis of nanoparticles by physical vapour deposition

Usually, metals or high vapour pressure metal oxides are evaporated from filaments boats of refractory metals like W, Ta and Mo in which the materials to be evaporated are held. Due to small particle interaction, bigger particles get formed. Therefore, they should be removed away as fast as possible from the source.

This is done by forcing an inert gas near the source, which removes the particles from the vicinity of the source. In general, the rate of evaporation and the pressure of gases inside the chamber determine the particle size and their distribution. Distance of the source from the cold finger is also important. Evaporated atoms and clusters tend to collide with gas molecules and make bigger particles, which condense on the cold finger.

While moving away from the source to the cold finger the clusters grow. If clusters have been formed on inert gas molecules, on reaching the cold finger, gas atoms or molecules may leave the particles there and then escape to the gas phase.

If reactive gases like O₂, H₂ and NH₃ are used in the system, evaporated material can interact with these gases forming oxide, nitride or hydride particles. Size, shape and even the phase of the evaporated material can depend upon the gas pressure in the deposition chamber. Clusters or nanoparticles condensed on the cold finger (water or liquid nitrogen cooled) can be scraped off inside the vacuum system.

The process of evaporation and condensation can be repeated several times until enough quantity of the material falls through a funnel in which a piston-anvil arrangement has been provided. One can even have separate low and high-pressure presses. A pressure of a few megapascals (MPa) to Giga pascal (GPa) is usually applied depending upon the material.

B. Laser Vaporization:

A powerful beam of laser evaporates the atoms from a solid source and atoms collide with inert gas atoms and cool on them forming clusters. They condense on the cooled substrate. The method is often known as laser ablation.

Gas pressure is very critical in determining particle size and distribution. Simultaneous evaporation of another material and mixing of the two evaporated materials in inert gas leads to the formation of alloys or compounds.

This method can produce some novel phases of the materials which are not normally formed. For example, Single Wall Carbon Nanotubes (SWNT) are mostly synthesized by this method. In this method, vaporization of the material is effected using pulses of the laser beam of high power.

The setup along with the interaction with the evaporation source is depicted in Figure 13.7. The setup is a high vacuum system equipped with an inert or reactive gas, laser beam, solid target and cooled substrate. Clusters of any material made of a solid target can be made are possible to synthesize. Usually, a laser operating in the UV range such as an excited monomer laser is necessary because other wavelengths like IR or visible are often reflected by surfaces of some metals.

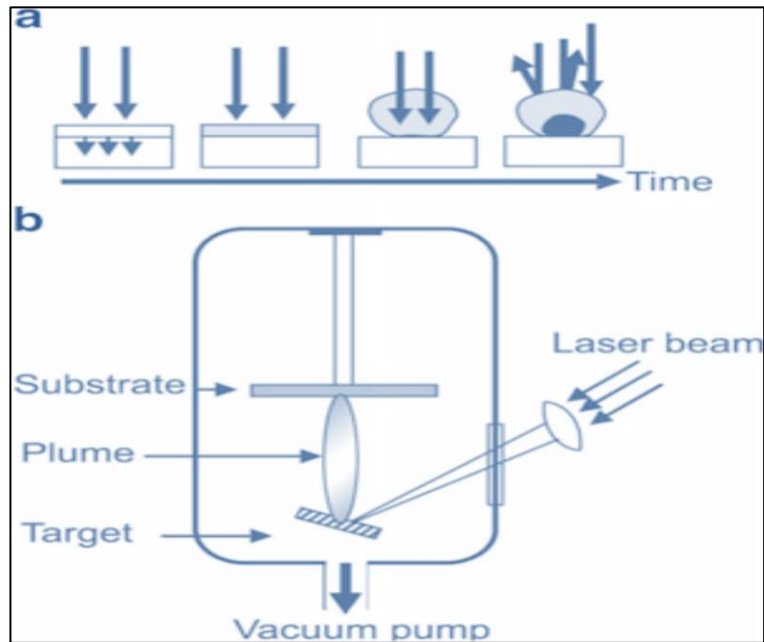


Figure 13.7: (a) Sequence of material evaporation by laser beam interaction with a target material. (b) Schematic Laser deposition

C. Laser Pyrolysis:

Another method of thin film synthesis using lasers is known as ‘laser pyrolysis’ shown in Figure 13.8. Here a mixture of reactant gases is decomposed using a powerful laser beam in presence of some inert gas like helium or argon. Atoms or molecules of decomposed reactant gases collide with inert gas atoms and interact with each other, grow and are then deposited on a cooled substrate.

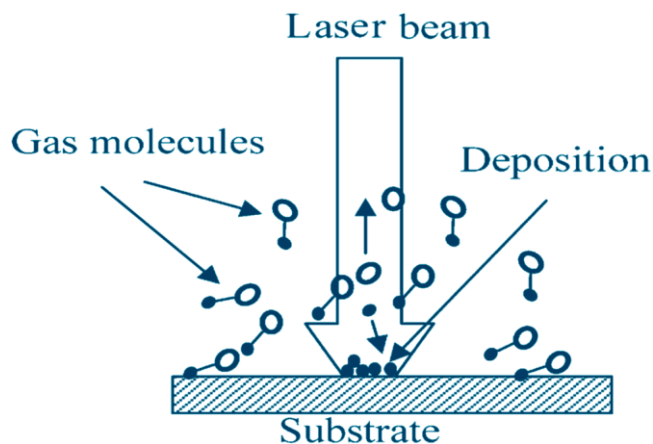


Figure 13.8: Schematic diagram of Laser Pyrolysis

Many nanoparticles of materials like Al_2O_3 and Si_3N_4 are synthesized by this method. Here gas pressure plays an important role in deciding the particle sizes and their distribution.

D. Ion Implantation:

Ion implantation involves the injection of very energetic ions into the surface of a solid substrate. The major components of an ion implantation facility are presented in Figure 13.9 and include a vacuum system, ion source, magnetic analyzer, accelerator, beam scanning, and target chamber.

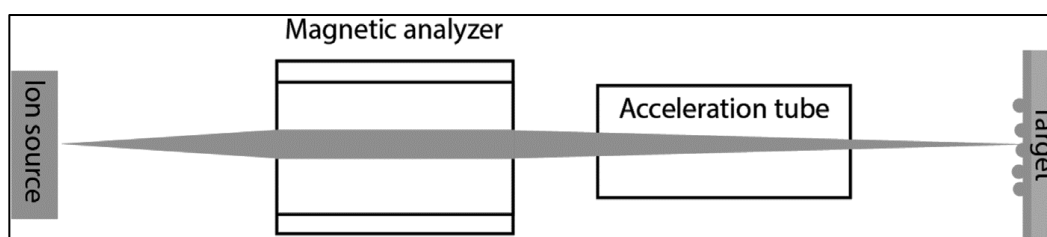


Figure 13.9: Schematic of ion implantation system

There are many examples in which high energy or low energy ions are used to obtain nanoparticles. It is possible to obtain single-element nanoparticles or compounds and alloys of more than one element. Post-annealing also is used sometimes to improve the crystallinity of the materials. In some experiments, it has been possible to even obtain doped nanoparticles using ion implantation. There is also a possibility of making nanoparticles using swift heavy ions employing high-energy ion accelerators like pelletrons.

Examples of ion implantation include the implantation of N to improve the wear resistance of metals and the implantation of Ti and C into Fe alloys to improve hardness and wear resistance. Ion implantation parameters can also be used to control nanocrystallite size distribution.

E. Plasma:

The plasma method is another method that is used to produce nanoparticles. Radiofrequency (RF) heating coils generate the plasma. The initial metal is enclosed in a pestle and the pestle is enclosed in an evacuated chamber.

The metal is then heated above its evaporation point by high voltage RF coils wrapped around the evacuated chamber. The gas that is used in the procedure is Helium (He), which forms a high-temperature plasma in the region of the coils after flowing into the system.

The metal vapour nucleates on the helium gas atoms and diffuses up to a cold collector rod, this is where nanoparticles are collected and are passivated by oxygen gas [17]. Classification of plasma methods based on the feeding materials to the reactor and also the heating source [Figures 13.10 and 13.11].

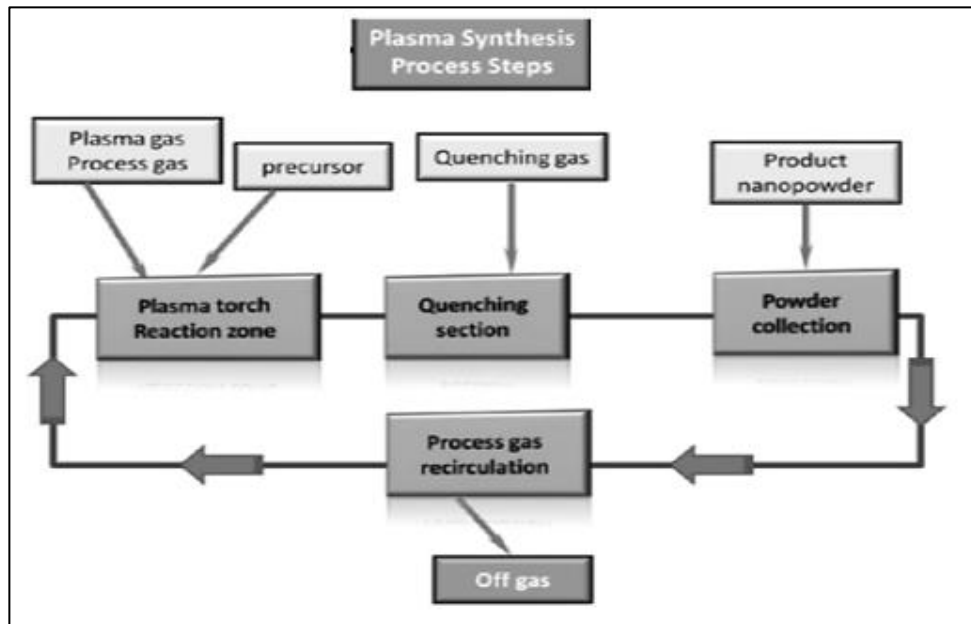


Figure 13.10: Flow diagram for production plant based on plasma burners

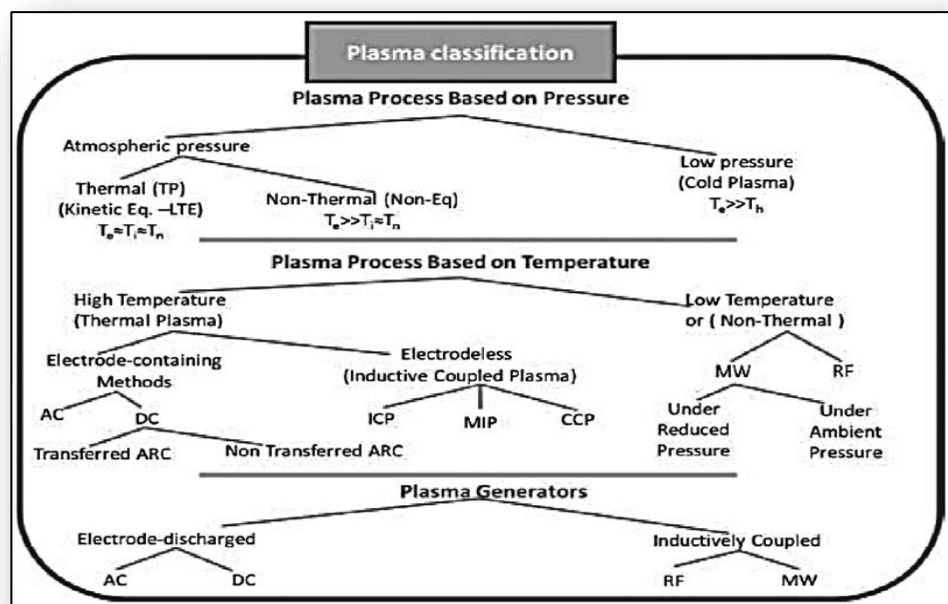


Figure 13.11. Different plasma classification

13.4.3 Chemical Methods:

A. Chemical Vapour Deposition (CVD):

CVD involves flowing a precursor gas or gases into a chamber containing one or more heated objects to be coated [Figure 13.12].

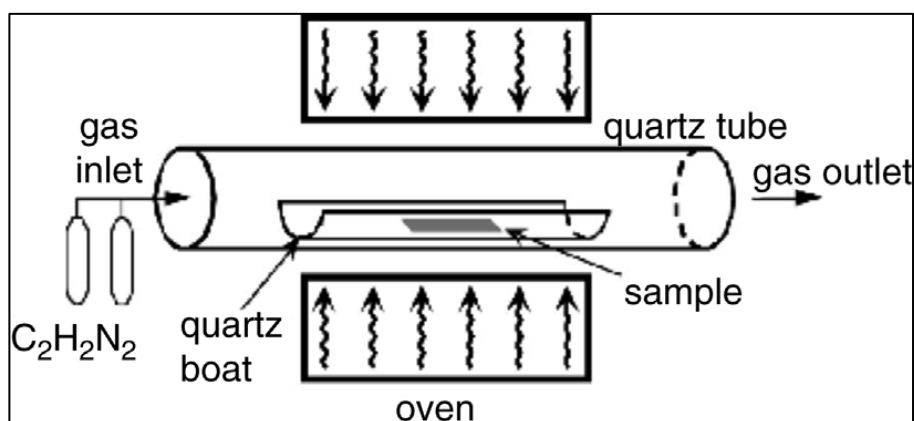


Figure 13.12: Schematics of a CVD Deposition Oven

The CVD method can synthesize ultrafine particles of less than 1 μm by the chemical reaction taking place in the gaseous phase. The reaction can be controlled to produce nanoparticles of sizes ranging from 10 to 100 nm [18, 19]. The basic CVD process can be considered as the transport of reactant vapour towards the substrate kept at some high temperature where the reactant cracks into different products, which diffuse on the surface, undergo some chemical reaction at the appropriate site, nucleate and grow to form the desired material film. The by-products created on the substrate have to be transported back to the gaseous phase removing them from the substrate. Vapours of desired material may be often pumped into the reaction chamber using some carrier gas. In some cases, the reactions may occur through aerosol formation in the gas phase. There are various processes such as reduction of gas, a chemical reaction between different source gases, oxidation or some disproportionate reaction by which CVD can proceed. There are two ways viz., hot wall and cold wall by which substrates are heated. In hot wall setup, the deposition can take place even on reactor walls. This is avoided in cold wall design. Besides this, the reaction can take place in the gas phase with a hot wall design, which is suppressed in a cold wall setup. Usually, gas pressures in the range of 0.1 to 1.0 torr are used. Growth rate and film quality depend upon the gas pressure and the substrate temperature. CVD is widely used in industry because of its relatively simple instrumentation, ease of processing, the possibility of depositing different types of materials and economic viability.

B. Electric Arc Deposition:

This is one of the simplest and most useful methods, which leads to the mass-scale production of fullerenes and carbon nanotubes. The positive electrode itself acts as the source of the material. Inert gas or reactive gas is necessary. Inert gas pressure is maintained

in the vacuum system. When an arc is set up, anode material evaporates. This is possible as long as the discharge can be maintained. By striking the arc between the two graphite electrodes, it is possible to get fullerenes in large quantities. In the case of fullerenes, the formation occurs at low helium pressure as compared to that used for nanotube formation. Also, fullerenes are obtained by purification of soot collected from the inner walls of the vacuum chamber, whereas nanotubes are found to be formed only at high He gas pressure and in the central portion of the cathode. No carbon nanotubes are found on the chamber walls.

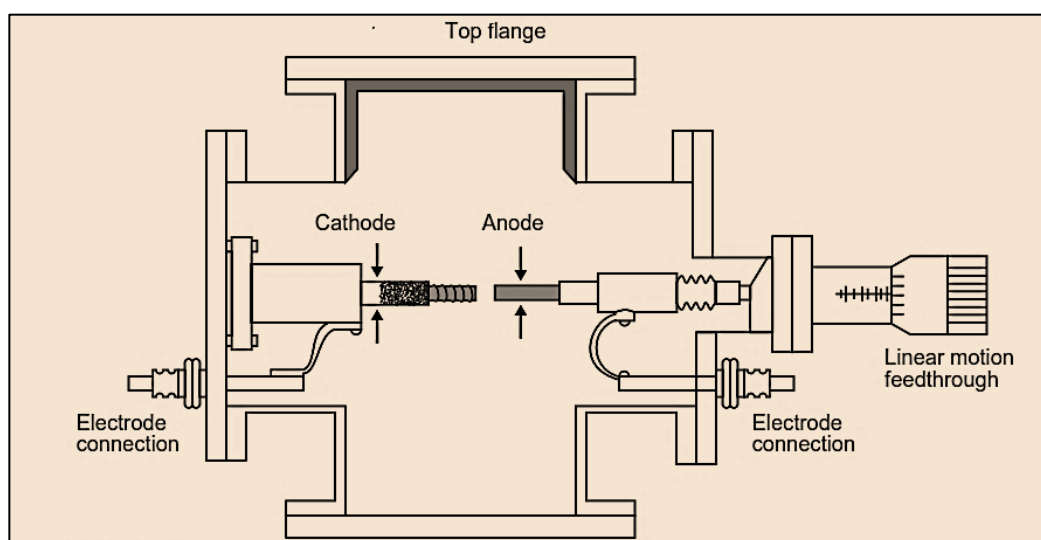


Figure 13.13: Schematic Illustration of the Method of Arc Discharge

Arc discharge was the method used to prepare multiwalled CNTs (MWCNTs) by Iijima in 1991 [20]. In this method, an AC plasma arc is generated between two electrodes maintained in an inert atmosphere as described in Figure 13.13.

The high temperature between the electrodes (3000-4000⁰C) causes sublimation of the carbon. The sublimated graphite is deposited at the negative electrode or the walls of the chamber where the process is carried out.

These deposits contain CNTs [21, 22]. For achieving the single-walled CNT (SWCNT) electrodes are doped with catalyst particles, such as Ni-Co, Co-Y, or Ni-Y [22-25]. Nanotubes produced by this method are generally entangled and have varying lengths. However, the tubes are of high quality with low amounts of defects.

C. Sol-Gel Method:

As the name implies sol-gel involves two types of materials ‘sol’ and ‘gel’. The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension and gelation of the sol to form a network in a continuous liquid phase [Figure 14] [26].

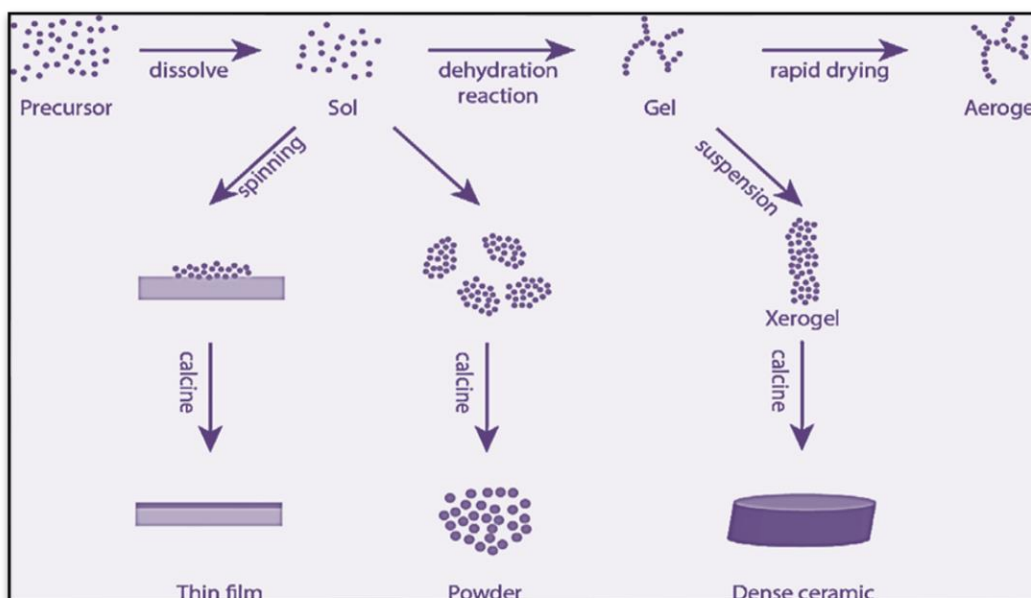


Figure 13.14: Schematic of the Sol-Gel Method

Synthesis of sol-gel, in general, involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes. Precursors are to be chosen so that they tend to form gels. Both alkoxides and metal salts can be used. Although only oxides do not need to be formed by a sol-gel process, often oxide ceramics are best synthesized by a sol-gel route. By polycondensation process sols are nucleated and ultimately sol-gel is formed.

The sol-gel method is particularly useful to synthesize ceramics or metal oxides although sulphides, borides and nitrides also are possible. All sol-gel formation process is usually low-temperature process. This means less energy consumption and less pollution too. It is also possible to synthesize nanoparticles, nanorods, nanotubes etc., using the sol-gel technique. Sols are solid particles in a liquid. They are thus a subclass of colloids. Gels are nothing but a continuous network of particles with pores filled with liquid.

D. Microemulsion:

An emulsion is a liquid in the liquid dispersion. A solution of polymers can produce emulsions as it is liquid. Emulsions are divided according to the size of the droplet, i.e., macro-emulsions, mini-emulsions, and micro-emulsions [27]. Micro-emulsion synthesis method is widely used for the production of inorganic nanoparticles [28]. Synthesis of nanoparticles in the cavities produced in a microemulsion is a widely used method. Whenever two immiscible liquids are stirred together, they are known to form what is called 'emulsion'. Whenever two immiscible liquids are stirred together, they are known to form what is called 'emulsion'. Emulsions are usually turbid in appearance. On the other hand,

there is another class of immiscible liquids, known as transparent microemulsions, and the droplets are in the range of ~1 to 100 nm. This is the size needed for the synthesis of nanomaterials. Microemulsions are stabilized using surfactants. When an organic liquid, water and surfactant are mixed, under some critical concentration, ‘micelles’ or inverse micelles are formed, depending upon the concentration of water and organic liquid. Micelles are formed with excess water and inverse micelles are formed more than organic liquid or oil. The ratio of water, oil and surfactant is important to decide which type of micelle will be formed and can be represented in a ternary phase diagram, using a triangle. The composition can be determined by drawing lines parallel to all three sides of the triangle.

The advantage of this method is the biocompatibility and biodegradability of synthesized materials. Biocompatibility is useful in drug delivery of nanomaterials and biodegradability is environmentally useful. Among different synthesis processes, the microemulsion method is one of the versatile preparation techniques that enable the control of particle properties such as size, geometry, morphology, homogeneity, and surface area [Figure 13.15] [29].

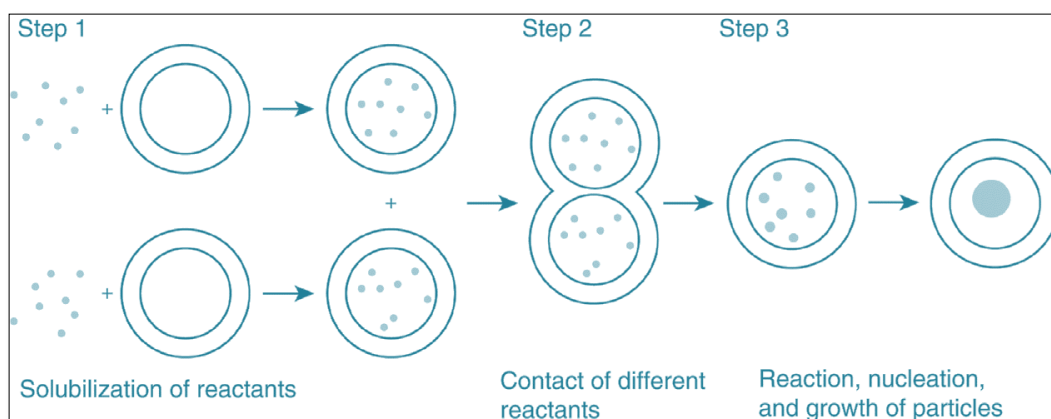


Figure 13.15: Synthesis of Microemulsions

13.5 Various Applications:

13.5.1 Food and Agriculture:

By using nanotechnology, the food industry can also be developed. For example, by using nanotechnology new functional materials and new instruments designed for food preservation and bio-security are developed. Bayer Company introduced airtight plastic packing with the help of nanotechnology.

Food is preserved in this plastic packing. From nanotechnology, genetic modifications in the constitution of the crop plant can be made. Nanotechnology revolutionizes the agriculture field in the part of absorbing nutrients, disease detection, disease control and smart delivery system [30]. In the future, nanocatalyst will be available in the pesticide and fertilizers to increase its efficiency at lower dosage levels, which protects the environment from high-dose pesticides.

13.5.2 Energy Harvesting:

Generate renewable resources are low-cost materials. NPs are widely used for the production of energy from the splitting of electrochemical water and photoelectrochemical [31]. At the nanoscale level, NPs can also store energy in different forms [32-34]. That is why they are used in energy storage applications [35]. Recently, Nanogenerators can convert mechanical energy into electrical energy by using piezoelectric.

13.5.3 Micro-Wiring:

In the electronic industry, metal nanoparticles are the best candidate for the manufacturing of a printed wired board [36]. The metal nanoparticles have less melting point than the bulk metals. By the conventional electric conduction paste, circuit formation is possible on polymer base material. Whenever particles are used at the nanoscale, the thickness of the wire is decreased to a nano level. The ink-jet method is very important for the formation of wiring at the nano level. The ink-jet method is not very expensive and it does not require long times like conventional techniques such as photolithographic methods and vacuum evaporation that are generally used. Metal nanoparticles paste can be prepared with gold. Gold is expensive that is why Copper is used as a substitute for it. Copper nanoparticles are used as antioxidants.

13.5.4 Electronics:

The interest in the progress of printed electronics has been growing for the last few years because of the high potential for low cost than the traditional silicon printed techniques. It is expected that electronics, which are printed with different inks, may rapidly flow. These inks may also contain CNTs, organics and ceramics nanoparticles [37]. One-dimensional semiconductors and metals have distinctive structural, electrical and optical properties which provide the key structural blocks for the development of electronic, photonic materials and sensors [38-40]. Nowadays, in the electronic industry, new semiconducting materials are discovered gradually. However, diodes and transistors even miniature chips are in use instead of vacuumed tubes [41].

13.5.5 Food Packaging:

Nanotechnology in the food packaging sector was accepted nowadays due to its tangible benefits. Currently, the widely used food packaging material is made of plastic like polyethene, polypropylene, polyvinyl alcohol, etc which are harmful and non-biodegradable. Another development in Nanotechnology in food packaging is carbon nanotubes which are cylindrical structures with nanoscale diameter. It improves the mechanical properties [42].

Nanosensors are sensors being added to the packaging material to detect the gases that rise off from the food when it's spoiled as well as prevent the permeation and transpiration of gases. Packaging materials with silica nanoparticles prevent oxygen penetration inside the package at the same time stops the moisture loss from the product [43].

13.5.6 Medicine:

Nanoscience and technology are currently have been developed in the field of medicine for detecting diseases such as cancer and atherosclerosis at early stages and targeted drug delivery for a cell or tissue of choice. Two important aspects of Nanotechnology in drug delivery systems release drugs and specifically target the diseased cells which improves the drug availability. Nanorobots, which could precisely occlude the specific sites on the teeth quickly, and permanent could prevent it within minutes. Nanosized organic and mineral phases can be an effective and new bone material for implantation because it has greater bone adhesion, durability and flexibility. A large surface-to-volume ratio, increases the bone cell interactions, thus improving the orthopaedic implant efficacy and minimising patient compliance [44].

13.5.7 Antimicrobial Activity:

Metal nanoparticles had anti-microbial activity, The bactericidal effect of metal nanoparticles is attributed owing to their small size as well as high surface-to-volume ratio, which allows them to interact closely with microbial membranes thus facilitating quick penetration of metal nanoparticles into the cell and excluding the internal components of the cell thus inactivate the microorganism. A disk diffusion test was carried out to find the minimum inhibitory effect.

13.5.8 Textiles:

The use of nanotechnology in the textile industry is attractive due to its distinctive and significant properties [45]. Some of the properties are water repellence, wrinkle resistance, anti-bacterial, anti-static and UV protection. Water repellence is imparted to the cotton material simply by a coating of a nano plasma over it [46]. Conventionally wrinkle resistance is done by resins but it leads to a decrease in dyeability, the tensile strength of fibre and abrasion resistance, could be prevented by titanium nanocatalyst and silica nanocatalyst for cotton and silk respectively [47].

13.6 Conclusions:

Nanoscience is the study of materials that exhibit remarkable properties, functionality and phenomena due to the influence of small dimensions. Today's nanotechnology harnesses current progress in chemistry, physics, material science, biotechnology and electronics to create novel materials that have unique properties because their structures are determined on the nanometer scale. Some of these materials have already found their way into consumer products, such as sunscreens and stain-resistant plants.

Various methods of preparation of nanoparticles have been developed and they are suitable for the synthesis of nanoparticles in different sizes and shapes. Nanomaterials possess high surface areas, magnetism, quantum effects, antimicrobial activity, and high thermal and electrical conductivities. The nanomaterial family includes carbon-based nanomaterials, nanoporous materials, core-shell materials, ultrathin 2-dimensional nanomaterials, and metal-based nanomaterials.

More focus is currently being placed on producing nanomaterials with controlled morphologies and nanoscale dimensions to achieve the desired outcomes because of well-organized nanostructures. By using nanotechnology, some commercial devices have already been introduced. Nanocatalyst provides an extremely attractive platform in nanotechnology.

The field of nanobiotechnology is very dynamic and the biosynthesis of nanoparticles using different microorganisms and plants is the focused area of current research. The biosynthesis of nanoparticles is a cost-effective and environmentally friendly alternative to chemical and physical methods. Biosynthesis of nanoparticles has a great potential in nanoparticle production as this method is free from toxic and hazardous chemicals used in conventional physical and chemical methods and is less expensive.

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ABOUT THE BOOK

Compared with conventional technologies and sciences, the development of nanoscience and nanotechnology dealing with the synthesis and characterization of nanostructure materials has been quite rapid and intensive, while also unprecedented. Now the technologies based on nanoscience and nanotechnology are exerting a profound and strong impact on every field of conventional technology and science.

In fact, all different scientific disciplines, including every single sector (such as nanomaterials, micro and nanomachines, micro and nanoelectronics), have their own paradigm. This is why innovations and industrial developments are profoundly different. However, these fields are strongly interlinked. It is therefore necessary to make our studies more interdisciplinary in order to enable us to understand the nanoworld.

Nano sciences and nanotechnologies are leading to a major turning point in our understanding of nature. Such a force has its consequences or in the words of a famous fictional character: every force has its dark side. Our future depends on how we use new discoveries and what risks they bring upon humanity and our natural environment. The ethical implications of this must therefore be discussed.

This book presents the possible applications of nano-sized materials in environmental processes. It is by far the most reliable guideline for the selection of nanomaterials to improve the efficiency of environmental processes and for designing nanomaterials for specific environmental processes and pollutants. The impact of nanomaterials on the environment has also been discussed in the book to help avoid causing secondary contamination by use of nanomaterials and to provide proper information about nanomaterials to potential users who wish to use and apply them in environmental technology.



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