GREEN SYNTHESIS OF CERIUM OXIDE NANOPARTICLES USING *Sauropus androgynus* LEAF EXTRACT AND STUDY OF OPTICAL PROPERTIES

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Abstract

Plants produce more stable nanoparticles compared to other chemical methods. The process of green synthesis is more efficient, simpler, and economical and can easily be scaled up to perform larger operations. Biological methods for nanoparticles synthesis using micro organisms, enzymes , and plant extract. In this project, I synthesized nanostructured cerium oxide particles by green synthesis. Highly stable and face centered cubic structured cerium oxide nanoparticles are produced by using Sauropus androgynus leaf extract and Cerium nitrate hexahydrate. Structural and optical properties of the synthesized nanoparticles have been characterized by UV-Vis spectrophotometer, FTIR, EDX and XRD analysis. The particles have been predominantly face centerd cubical structure and particle size could be controlled by varying the concentrations of leaf extract solution.

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CHAPTER I

INTRODUCTION

1.1 Nanoscience

"Nanoscience" is the emerging science of objects that are intermediate in size between the largest molecules and the smallest structures that can be fabricated by current photolithography; that is, the science of objects with smallest dimensions ranging from a few nanometres to less than 100 nanometres [1-3]. Nanoscience is concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties. phenomena and processes, because of their small nanoscale size. Structural features in the range of about 10 Å to 1000 A, determine important changes as compared to the behaviour of isolated molecules (10A) or of bulk materials (>0.1 μm). Nanoscience aims to understand the novel properties and phenomena of nano based entities. The linguistic form nano originates from the classical Latin namus or its ancient Greek etonym nanos meaning "dwarf". In 1958, nano, together with giga, tera, and pico, was adopted in the newly formed International System of units. In 1974, Norio Taniguchi introduced the term nanotechnology at an engineering conference in Tokyo. Feynman's lectures or Norio Taniguchi's original use of the term "nanotechnology" are often cited as the starting points for the concept, scientists have long investigated nanoscale materials and wondered about the nature of materials on small length scales [4].

1.2 Nanotechnology

Nano technology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials, as well as fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures [4]. According to National Science Foundation and NNI. nanotechnology is the ability to understand, control, and manipulate matter at the level of individual atoms and molecules, as well as at the "supramolecular" level involving clusters of molecules (in the range of about 0.1 to 100 nm), in order to create materials, devices, and systems with fundamentally new properties and functions because of their small structure. [5]. Nanotechnology aims to gain control of structures and devices at the atomic, molecular and supramolecular levels, and to learn how to efficiently manufacture and use these devices.

The idea of nanotechnology started in the 1950s, though the name wasn't invented until 1974. In a way, though, nanotechnology has been around for centuries. After all, a lot of chemistry is about controlling nanoscale objects atoms and molecules and since ancient times, artists

have used the special properties of gold and other metal nanoparticles to color glass, but without knowing about nanoparticles. In recent years, nanotechnology has become one of the most important and exciting forefront fields in Physics, Chemistry, Engineering and Biology. It shows great promise for providing us in the near future with many breakthroughs that will change the direction of technological advances in a wide range of applications. The WTEC study concluded that this technology has enormous potential to contribute to significant advances over a wide and diverse range of technological areas ranging from producing stronger and lighter materials, to shortening the delivery time of nano structured pharmaceuticals to the body's circulatory system, increasing the storage capacity of magnetic tapes, and providing faster switches for computers. Recommendations made by this and subsequent panels have led to the appropriation of very high levels of finding in recent years. The research area of nanotechnology is interdisciplinary, covering a wide variety of subjects ranging from the chemistry of the catalysis of nanoparticles, to the physics of the quantum dot laser [6].

1.3 History of Nanoscience and Nano Technology

Today's widespread activities in nanoscience and technology are actually rooted in the ideas of some leading scientists of the last century. Among them, the foremost name was Richard P. Feynman. He delivered a legendary talk entitled "there is plenty of room at the bottom" in the Annual general body meeting of the American Physical society on December 29, 1959 (1) at California Institute of Technology. In that talk he discussed about the ideas of manipulating and controlling things at the atomic scale. In this famous lecture the great scientist uttered also these famous words "the principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom". He also envisioned building circuits having sizes few nanometres that can be used as elements in more powerful computers. In that time these ideas were regarded "too speculative". But nearly twenty years later from this prophetic talk, many inventions and discoveries began to appear justifying Feynman's time ahead ideas. Soon the technology advisors and predictors realized the importance of these discoveries and declared that a new revolution is imminent namely nanotechnology, just as in the past we experienced industrial revolution and information revolution. Drexler expanded Feynman's ideas and definition in a stimulating and lateral thinking way in his book, 'Engines of Creation, the Coming Age of Nanotechnology'. Drexler to have some ideas about nanotechnology: "Nanotechnology is the principle of manipulation atom by atom, through control of the structure of matter at the molecular level. It entails the ability to build molecular systems with atom-by-atom precision, yielding a variety of nano machines." In recognition with this reality National Science and Technology Council (NSTC) of USA created an integrating working group on nanoscience, engineering and technology in 1998. Then in the year 2001 they

announced the National Nanotechnology Initiative (NNI) programme with a large amount of fund in the budgetary provisions. The major objective of this initiative was to create a common platform for the academia, industries and also private sector for working on this new technology. Following this example, most of the advanced countries in the world and many developing countries including China and India invested heavily on research and development in this new field of science and technology.

Add photos in 1867, James Clerk Maxwell put forward some of the important and leading concept about nanotechnology. Later the concept of a "nanometre" was first proposed by Richard Zsigmondy, the 1925 Nobel Prize Laureate in chemistry. He coined the term nanometre explicitly for characterizing particle size and he was the first to measure the size of particles such as gold colloids using a microscope. Modern nanotechnology was the brain child of Richard Feynman, the 1965 Nobel Prize Laureate in physics. During the 1959 American Physical Society meeting at Caltech, he presented a lecture titled, "There's Plenty of Room at the Bottom", in which he introduced the concept of manipulating matter at the atomic level. This novel idea demonstrated new ways of thinking and Feynman's hypotheses have since been proven correct. It is for these reasons that he is considered the father of modern nanotechnology. Almost 15 years after Feynman's lecture, a Japanese scientist, Norio Taniguchi, was the first to use "nanotechnology" to describe semiconductor processes that occurred on the order of a nanometre. He advocated that nanotechnology consisted of the processing, separation, consolidation, and deformation of materials by one atom or one molecule. The golden era of nanotechnology began in the 1980s when Kroto, Smalley, and Curl discovered fullerenes and Eric Drexler of Massachusetts Institute of Technology (MIT) used ideas from Feynman's "There is Plenty of Room at the Bottom" and Taniguchi's term nanotechnology in his 1986 book titled, "Engines of Creation: The Coming Era of Nanotechnology." Drexler proposed the idea of a nanoscale "assembler' which would be able to build a copy of itself and of other items of arbitrary complexity. Drexler's vision of nanotechnology is often called "molecular nanotechnology." The science of nanotechnology was advanced further when lijima, another Japanese scientist, developed carbon nanotubes. The beginning of the 21st century saw an increased interest in the emerging fields of nanoscience and nanotechnology. In the United States, Feynman's stature and his concept of manipulation of matter at the atomic level played an important role in shaping national science priorities. President Bill Clinton advocated for funding of research in this emerging technology during a speech at Caltech on January 21, 2000. Three years later, President George W. Bush signed into law the 21st Century Nanotechnology Research and Development Act. The legislation made nanotechnology research a national priority and created the National Technology Initiative (NNI). Today, the NNI is managed within a framework at the top of which is the President's Cabinet-level National Science and Technology Council (NSTC) and

its Committee on Technology. The Committee's Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) is responsible for planning, budgeting, implementation, and review of the NNI and is comprised of representatives from 20 US departments and independent agencies and commissions [6].

Medieval Stained Glass

Figure 1.1 Medieval stained glass

1.4 Definition of Nano Science and Nano Technology

The origin of the term "nano" comes from the Greek word for dwarf, but in scientific jargon, "nano" means one billionth. One nanometre (abbreviated a 1nm) is 1/1000,000,000 of a meter. Nanotechnology is the understanding and control of matter at the nanoscale, at dimensions between approximately 1 and 100 nanometres, where unique phenomena enable novel applications. Matter can exhibit unusual physical, chemical, and biological properties at the nanoscale, differing in important ways from the properties of bulk materials, single atoms, and molecules. Some nanostructured materials are stronger or have different magnetic properties compared to other forms or sizes of the same material. Others are better at conducting heat or electricity. They may become more chemically reactive, reflect light better, or change color as their size or structure is altered.

Although modern nanoscience and nanotechnology are relatively new, nanoscale materials have been used for centuries. Gold and silver nanoparticles created colors in the stained-glass windows of medieval churches hundreds of years ago. The artists back then just didn't know that they were using nanotechnology to create these beautiful works of art!

Nanotechnology encompasses nanoscale science, engineering, and technology in fields such as chemistry, biology, physics, materials science, and engineering [7].

1.5 Nanoparticles

A nanoparticle or ultrafine particle is usually defined as a particle of matter that is between 1

and 100 nanometres (nm) in diameter. The term is sometimes used for larger particles, up to 500 nm, or fibres and tubes that are less than 100 nm in only two directions. At the lowest range, metal particles smaller than 1 nm are usually called atom clusters instead. Nanoparticles are usually distinguished from micro particles (1-1000 um). "fine particles" (sized between 100 and 2500 nm), and "coarse particles" (ranging from 2500 to 10,000 nm), because their smaller size drives very different physical or chemical properties, like colloidal properties and optical or electric properties. Being more subject to the Brownian motion, they usually do not sediment, like colloidal particles that conversely are usually understood to range from 1 to 1000 nm. Being much smaller than the wavelengths of visible light (400- 700 nm), nanoparticles cannot be seen with ordinary optical microscopes, requiring the use of electron microscopes or microscopes with laser. For the same reason, dispersions of nanoparticles in transparent media can be transparent, whereas suspensions of larger particles usually scatter some or all visible light incident on them. Nanoparticles also easily pass through common filters, such as common ceramic candles, so that separation from liquids requires special nano filtration techniques [8].

The properties of nanoparticles often differ markedly from those of larger particles of the same substance. Since the typical diameter of an atom is between 0.15 and 0.6 nm, a large fraction of the nanoparticle's material lies within a few atomic diameters from its surface. Therefore, the properties of that surface layer may dominate over those of the bulk material. This effect is particularly strong for nanoparticle dispersed in a medium of different composition, since the interactions between the two materials at their interface also becomes significant [9].

1.6 Classification of Nanomaterials based on origin

1.6.1 Natural Nanomaterials:

Natural nanomaterials are produced in nature either by biological species or through anthropogenic activities. The production of artificial surfaces with exclusive micro and nanoscale templates and properties for technological applications are readily available from natural sources. Naturally occurring nanomaterials are present through the Earth's spheres (i.e., in the hydrosphere, atmosphere, lithosphere and even in the biosphere), regardless of human actions. Earth is comprised of nanomaterials that are naturally formed and are present in the Earth's spheres, such as the atmosphere, which includes the whole of troposphere, the hydrosphere, which includes oceans, lakes, rivers, groundwater and hydrothermal vents, the lithosphere, which is comprised of rocks, soils, magma or lava at particular stages of evolution and the biosphere, which covers microorganisms and higher organisms, including humans[9].
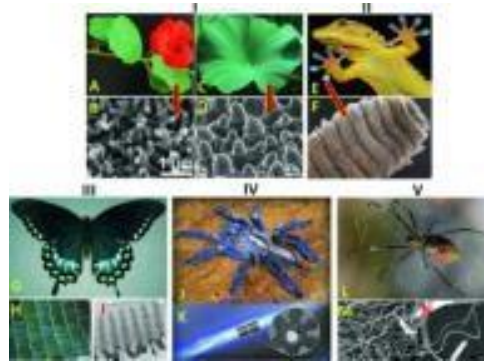
Figure 1.2 Photograph and SEM image of different organisms

1.6.2 **Synthetic Nanomaterials:**

Synthetic (engineered) nanomaterials are produced by mechanical grinding. engine exhaust and smoke, or are synthesized by physical, chemical, biological or hybrid methods. The question of risk assessment strategies has arisen in recent times as there is increased fabrication and subsequent release of engineered nanomaterials as well as their usage in consumer products and industrial applications. These risk assessment strategies are highly helpful in forecasting the behaviour and fate of engineered nanomaterials in various environmental media. The major challenge among engineered nanomaterials is whether existing knowledge is enough to forecast their behaviour or if they exhibit a distinct environment related behaviour, different from natural nanomaterials. Currently, different sources related to potential applications are used for the production of engineered NMs [10].
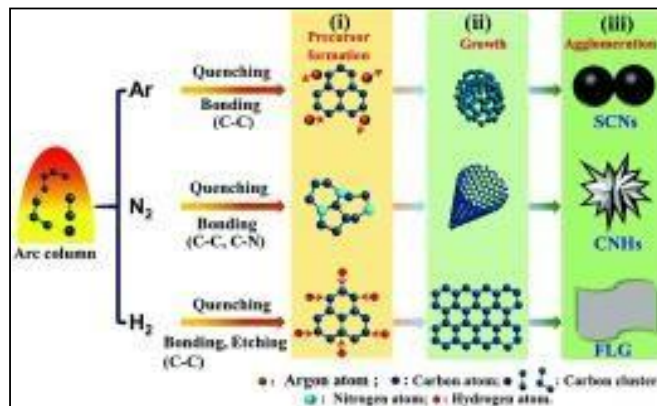
Figure 1.3 Some examples of Synthetic nanomaterials

1.7 **Classification of Nanomaterials based on the number of dimensions**

Nanostructured materials are classified as: zero-dimensional (OD (ID), two dimensional (2D) and three-dimensional (3D) nanomaterials. Zero-dimensional nanomaterials: Here, all dimensions (x, y, z) are at nanoscale, i.e. no dimensions are greater than 100 nm, electrons in OD NMs are entrapped in a dimensionless space. It includes graphene quantum dots (GQDs),

carbon quantum dots (CQDs), fullerenes, inorganic quantum dots (QDs), magnetic nanoparticles (MNPs), noble metal nanoparticles, up conversion nanoparticles (UCNPs) and polymer dots (Pdots)

1.7.1 One-dimensional nanomaterials:

Here, two dimensions (x, y) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials. Electrons are confined within two dimensions, indicating electrons cannot move freely. These 1-D nanomaterials can be amorphous or crystalline; single or poly crystalline, and metallic, ceramic, or polymeric. Examples include nanotube, nanofiber, nanowire and nanorod, and nanofilaments [11].
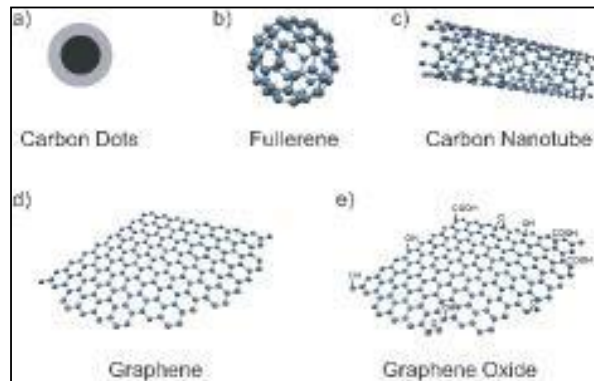
Figure 1.4 Classification of nanomaterials

1.7.2 Two-dimensional nanomaterials:

Here, one dimension (x) is at nanoscale and the other two are outside the nanoscale. The 2D nanomaterials exhibit plate like shapes. It includes nanofilms, nanolayers and nano coatings with nanometer thickness. Examples include graphene, hexagonal boron nitride (hBN), and metal dichalcogenides (MX_2) [11].
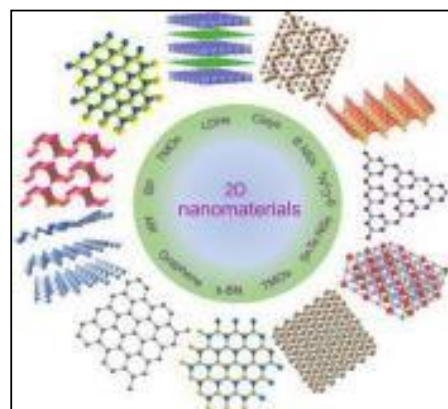
Figure 1.5 Two dimensional nanomaterial

1.7.3 Three-dimensional nanomaterials:

These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100 nm. The bulk (3D) nanomaterials are

composed of a multiple arrangement of nano size crystals in different orientations. It includes dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multinanolayers (polycrystals) in which the OD, 1D and 2D structural elements are in close contact with each other and form interfaces [11].

1.8 Classification of Nanomaterials based on Materials

1.8.1 Carbon-Based Nanomaterials

These types of nanomaterials are made up of carbon content and have various morphologies. The carbon-based nanomaterials can be hollow tubes or spheres, carbon nanofibers, Fullerenes, and graphene. The different methods used for the synthesis of carbon-based nanomaterials include chemical vapour deposition (CVD), arc discharge, and laser ablation.

(a) Fullerenes:

Fullerenes (C60) are spherical carbon molecules made up of carbon atoms arranged in sp2 hybridization. Fullerenes contain 28-1500 carbon atoms arranged in spherical structures with a diameter of up to 8.2nm for a single layered fullerene and 4 36nm for a multi-layered fullerene.

(b) Graphene:

This is the carbon-containing network. The arrangement of carbon atoms forms a hexagonal pattern in the graphene network and makes two dimensional planar surfaces. The thickness of a two-dimensional sheet is about 1 2nm.

(c) Carbon Nano tubes (CNTs):

These are nanofoils made up of carbon containing graphene. The carbon atoms are arranged in honeycomb lattice in carbon nanotubes and form hollow cylinders of 0.7nm diameter for a single layered CNT and about 100nm for a multi-layered CNT. The length of CNT varies from a few um to a few mm.

(d) Carbon nanofibers:

The graphene nanofoils used in the production of carbon nanofibers are the same as CNTs but the structure is different. The graphene molecules are arranged in cone or cup form rather than the regular cylindrical tubes of CNTs.

(e) Carbon black: This is an amorphous nanomaterial made up of carbon atoms that are arranged in a spherical shape with diameters from 20 to 70nm. The carbon black particle-particle interaction is so high that they bind with each other and form aggregates around 500nm.

1.8.2 Inorganic-Based Nanomaterials

It is these nanomaterials that make up metals and metal oxides. They can be synthesized from

metals such as Ag, Au, and Fe: and the metal oxides are TiO2, ZnO, and MnO2. Semiconductor nanomaterials are also synthesized from silicon and ceramic materials.

1.8.3 Organic-Based Nanomaterials

The organic-based nanomaterials are made up of organic matter other than carbon and inorganic material. The synthesis of these nanomaterials is through self-assembly or transformation from organic matter into the desired structure. The noncovalent (weak) interaction applies in these types of materials.

1.9 Composite-Based Nanomaterials

Composite nanomaterials are made up of one more layer of nanoparticles. These nanomaterials are combined with other nanoparticles, bulk materials, or more complex materials like metal frameworks. The composites may be made up of many types of materials such as metal, ceramic, organic, inorganic, carbon-based, or bulk polymers. These materials have different morphologies depending on the synthesis and required properties for the desired applications [12].

1.9.1 Nanocomposites

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometres (nm) or structures having nano scale repeat distances between the different phases that make up the material. The idea behind Nanocomposite is to use building blocks with dimensions in nanometre range to design and create new materials with unprecedented flexibility and improvement in their physical properties. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component material [13].

Nanoclay-based polymeric nanocomposites are among the first composites to be launched in the market as improved packaging tools. They have been developed from thermoplastic polymer fabricated with clay nanoparticles, which include nylons, polyamides, polystyrene, polyolefin, polyurethane, epoxy resins, polyimides, and polyethylene terephthalate. These are often used for nanoclay based multilayer film packaging of beverages, beers, carbonated drinks, and edible oils. Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio [13].

1.10 <u>Synthesis Methods of Nanomaterials</u>

The synthesis of nanomaterials is a key to the future success of this new technology and in principle; the approaches to the synthesis of nanomaterials can be divided into two main classes: Top-down approaches and bottom-up approaches.

1.10.1 <u>Top-down approach</u>

Top-down approach involves the breaking down of the bulk material into nanosized structures or particles. Top-down synthesis techniques are extension of those that have been used for producing micron sized particles. Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties. The biggest problem with the top-down approach is the imperfection of surface structure. For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on its surface. Examples of such techniques are high energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, etc. [14].

Many top-down mechanical methods are utilized by industry. Thermal methods form a nebulous category and we try and focus on those that provide heat to a fabrication process. Of these, electrospinning is a means to form nano thread materials. High energy methods are those that require an excessive input of energy

whether in the form of heat, electricity or solar energy. Are discharge being the first controlled means of making carbon nanotubes. Laser ablation and solar flux also work well. The problem is control of quality and potential upscale. Lithographic methods, as we all know quite well, although energy intensive and requiring expensive equipment and facilities are top-down methods capable of producing for the most part micron-sized features [14].
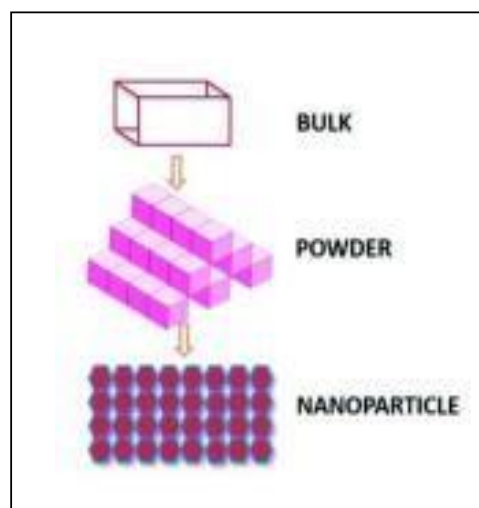

Figure 1.6 Top down approach

1.10.1.2 Examples for top-down approach

(a) Ball milling

Ball milling is a mechanical technique that is broadly used to grind powders into fine particles. The reactants are generally broken apart using solvent molecules in the traditional method; but in ball milling, reactants are broken by using mechanical forces. The term mechanochemistry has been introduced very recently. The use of ball milling in the synthesis and reactions of organic compounds have been published in many review articles. The application of solvent-free ball milling in organic synthesis is relatively rare. However, in the last decade, this technique has attracted growing interest because of its simplicity, low cost, and environment friendliness, as well as its capability to achieve very high yields. On the basis of these aspects, research will definitely increase in future in basic and applied science fields [15].
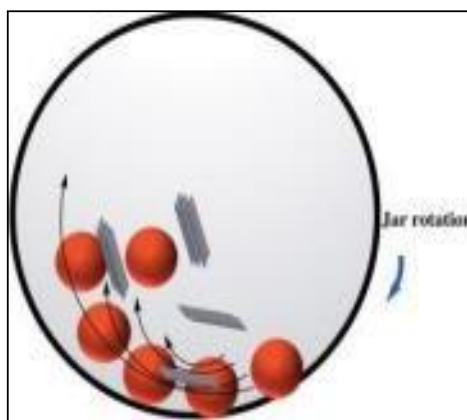
Figure 1.7 Ball milling process

(b) Electron Beam Lithography

Electron-beam lithography (often abbreviated as e-beam lithography, EBL) is the practice of scanning a focused beam of electrons to draw custom shapes on a surface covered with an electron-sensitive film called a resist (exposing). The electron beam changes the solubility of the resist, enabling selective removal of either the exposed or non-exposed regions of the resist by immersing it in a solvent (developing). The purpose, as with photolithography, is to create very small structures in the resist that can subsequently be transferred to the substrate material, often by etching. The primary advantage of electron-beam lithography is that it can draw custom patterns (direct-write) with sub-10 nm resolution. This form of mask less lithography has high resolution and low throughput, limiting its usage to photomask fabrication, low-volume production of semiconductor devices, and research and

development [16].

Figure 1.8 Electron beam Lithography

(c) Gas phase condensation

Gas-phase synthesis characterizes a class of bottom-up methods for producing multifunctional nanoparticles (NPs) from individual atoms or molecules. This review aims to summarize recent achievements using this approach, and compare its potential to other physical or chemical NP fabrication techniques. More specifically, emphasis is given to magnetron-sputter gas-phase condensation, since it allows for flexible growth of complex, sophisticated NPs, owing to the fast kinetics and non-equilibrium processes it entails. Nanoparticle synthesis is decomposed into four stages, i.e., aggregation, shell-coating, mass-filtration, and deposition. We present the formation of NPs of various functionalities for different applications, such as magnetic, plasmonic, catalytic and, gas-sensing, emphasizing on the primary dependence of each type on a different stage of the fabrication process, and their resultant physical and chemical properties [17].

1.10.2 Bottom-up Approach

The alternative approach, which has the potential of creating less waste and hence the more economical, is the 'bottom- up. Bottom-up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by cluster. Many of these techniques are still under development or are just beginning to be used for commercial production of nanopowders. Organometallic chemical route, revere-micelle route, sol-gel synthesis, colloidal precipitation. hydrothermal synthesis, template assisted sol-gel, electrodeposition etc., are some of the well-known bottom-up techniques reported for the preparation of luminescent nanoparticles [14].
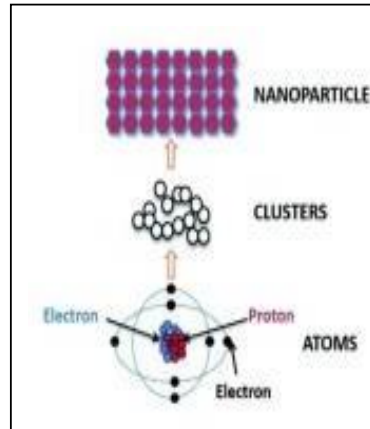
Figure 1.8 Bottom Up Apporach

1.10.2.1 Examples for Bottom-up approach

(i) Hydrothermal method

Hydrothermal method is a standard preparation route, especially for powdery nanostructure. Hydrothermal synthesis refers to the heterogeneous reactions for synthesizing inorganic materials in aqueous media above ambient temperature and pressure. In this case, an aqueous mixture of precursors is heated in a sealed stainless-steel autoclave above the boiling point of water, and consequently the pressure within the reaction autoclave is dynamically increased above atmospheric pressure. This effect of high temperature and pressure provides a one step process to produce highly crystalline materials without the need of post annealing treatment. The hydrothermal synthesis could obtain magnetic nanomaterials with very high crystallinity due to their high temperature and high-pressure reaction conditions. Hydrothermal method has several advantages such as low cost, easy experimental setup, and high yield. As a result of the main thermodynamic and kinetic features of the hydrothermal process, the main advantages of the hydrothermal synthesis are:

• One step process for powder synthesis or oriented ceramic films.

• Minimized consumption of energy, particularly for complex and doped oxides.

 • Products with much high homogeneity than solid state processing.

 • One of the few methods enabling for obtaining of controlled doped or complex material system.

Figure 1.9 Hydrothermal Process

(ii) Sol-gel Synthesis

The sol-gel process is a more chemical method (wet chemical method) for the synthesis of various nanostructures, especially metal oxide nanoparticles. In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis. Since the gel obtained from the hydrolysis/alcoholysis process is wet or damp, it should be dried using appropriate methods depending on the desired properties and application of the gel. For example, if it is an alcoholic solution, the drying process is done by burning alcohol. After the drying stage, the produced gels are powdered and then calcined. The sol gel method is a cost-effective method and due to the low reaction temperature there is good control over the chemical composition of the products. The sol gel method can be used in the process of making ceramics as a molding material and can be used as an intermediate between thin films of metal oxides in various applications. The materials obtained from the sol-gel method are used in various optical, electronic, energy, surface engineering, biosensors, and pharmaceutical and separation technologies (such as chromatography). The sol-gel method is a conventional and industrial method for the synthesis of nanoparticles with different chemical composition. The basis of the sol-gel method is the production of a homogeneous sol from the precursors and its conversion into a gel. The solvent in the gel is then removed from the gel structure and the remaining gel is dried. The properties of the dried gel depend significantly on the drying method. In other words, the "removing solvent method" is selected according to the application in which the gel will be used. Dried gels in various ways are used in industries such as surface coating, building insulation, and the production of special clothing. It is worth mentioning that, by grinding the gel by special mills, it is possible to achieve nanoparticles [18].
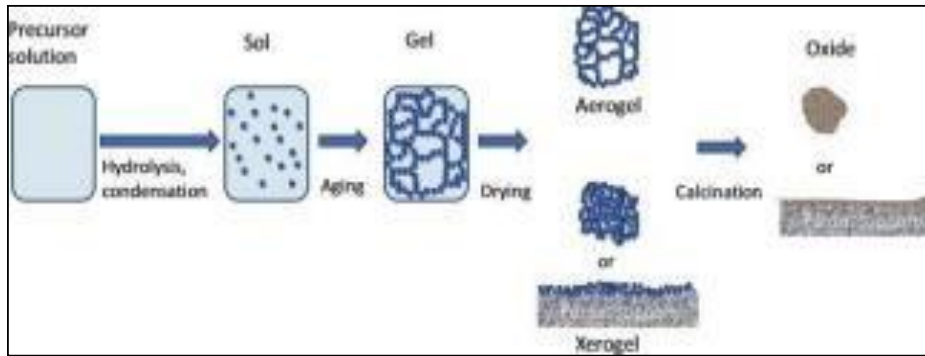
Figure 1.10 Sol gel Process

(iii) Electrodeposition

Electrodeposition is a flexible low-cost method of fabrication of a wide variety of two- and three-dimensional materials such as coatings and films. The principles of the electrodeposition process are based on principles of electrochemical phenomena associated with the reduction or deposition of electroactive and accompanying species on the cathode surface. This would make the electrodeposition process more controllable if one considers the electrochemical principles into account for target purposes and applications. However, many empirical factors in designing and controlling of electrodeposition process exist. Anticorrosion coatings have been a major part of corrosion protection tools employed for years. Electrodeposition is one successful method to fabricate coatings. Thanks to remarkable advances in nanoscience and nanotechnology and exotic effects of the nanoscale size on properties and functionalities of materials. electrodeposition of nanocoatings has become an interesting subject of research recently. In this chapter, the electrodeposition of anticorrosion nanocoatings is described. After a brief overview of the electrodeposition, two types of nanocoatings including nanocomposites and nanocrystalline, their electrodeposition principles, and corrosion behaviour based on conventional electrochemical studies are explained [19].
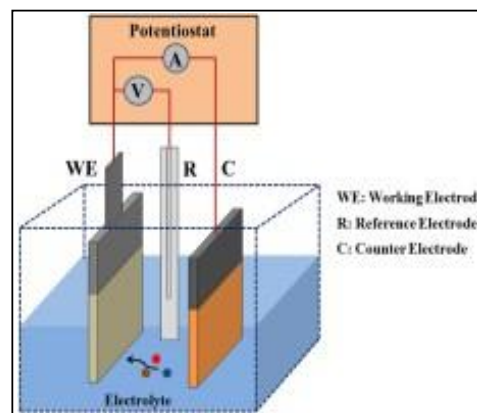

Figure 1.11 Electrodeposition

CHAPTER 2

LITERATURE REVIEW

Charbgoo *et al.* synthesised ceriun nanoparticles by green synthesis method for biological applications Plant-mediated synthesis of CeO_2-NPs of metal and metal oxide NPs. Recently, phytosynthesis of CeO_2-NPs was reported using different plants, such as *Gloriosa superba*, *Acalypha indica* and even *Aloe vera* plant leaf extract (Figure 1).[33–35] The plant extracts acted as stabilizing and capping agents in the CeO_2-NPs synthesis process. Investigating biological effects of the phytosynthesized NPs, antibacterial activity of them was examined. The results showed that smaller crystal sizes with a higher surface area led to higher antibacterial activity. These reports applied bio-directed methods of CeO_2-NP synthesis. Phytosynthesis However, the synthesized nanoparticles were generally so large in size that, according to literature, they were not appropriate for biomedical applications.[1,36] Recently, biosynthesis of NPs using yeast and fungi has also been noted. Munusamy et al had explained rapid and extracellular synthesis of cerium oxide NPs using fungus *Curvularia lunata* culture media.[37] The synthesized NPs had a cubic structure and exhibited antibacterial effects against different kinds of bacteria.[37] It is known that CeO_2-NPs cannot enter bacterial and algal cells[30].

Ali Es-Haghi *et al.* Cerium oxide nanoparticle (CeO-NP) was synthesized using *Origanum majorana* L. leaf extract and characterized using particle size analyzer, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Fourier transform infrared (FTIR). The antioxidant properties and cytotoxic effects of CeO-NP in human breast carcinoma cells (MDA-MB-231 cell line) and human umbilical vein endothelial cells (HUVEC) as normal cells were evaluated. To determine the probable molecular mechanism of action of CeO-NP on cellular redox and anti-inflammatory potential, the expressions of antioxidant-related genes catalase (CAT), superoxide dismutase (SOD) in HUVEC cell line were also analyzed. The results indicated that spherically shaped nanoparticles with a size of 10–70 nm bound to functional phenolic and flavonoids from *O. majorana* L. leaf extract. The green synthesized CeO-NP showed antioxidant activity by free radical scavenging activity against DPPH and ABTS free radicals. The antioxidant activity was significantly ($p < 0.001$) lower than that of Butylated hydroxyanisole (BHA) as a reference antioxidant [31].

Muthuvel *et al.* The eco-friendly synthetic approach for preparing CeO$_2$-NPs using *C. procera* flower extract. The synthesized CeO$_2$-NPs were studied for their UV–Vis, XRD and HR-TEM. The X-ray diffraction studies confirmed the cubic structure of synthesized CeO$_2$-NPs with an average crystallite size of 7 nm. High Resolution Transmission Electron Microscope (HR-TEM) images showed that the CeO$_2$-NPs possessed spherical shape and particle size of 21 nm. The photocatalytic degradation of methyl orange (MO) dye under sunlight irradiation by biosynthesized CeO$_2$-NPs was analyzed. The synthesized CeO$_2$-NPs exhibited 98% degradation activity against MO dye. Furthermore, antibacterial activity of *C. procera* flower extract and biosynthesized CeO$_2$-NPs were studied. The biosynthesized CeO$_2$-NPs exhibits a important antibacterial activity against Gram negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa* than Gram positive bacteria.[32]

Altaf *et al.*cerium oxide nanoparticles (CeO$_2$-NPs) were synthesized using *Acorus calamus* aqueous extract and tested for the antibiofilm activity both against Gram +ve and Gram −ve bacteria. The average size of synthesized CeO$_2$-NPs was found to be 22.03 nm. The biofilms of the test bacteria were inhibited by more than 75% by the treatment with CeO$_2$-NPs. The quantitative biofilm data were further verified by light microscopy, electron microscopy, and confocal microscopy. The confocal and electron microscopic analysis confirmed that treatment with CeO2-NPs reduced the development and colonization of the bacteria on solid support. Moreover, it was found that the colonization and biofilm development by test bacteria were fairly reduced on the glass surface. Moreover, a dose-dependent inhibition of preformed biofilms was also found. The exopolysaccharides (EPS) production by the test bacteria were substantially reduced by the supplementation of CeO$_2$-NPs in culture media. The findings of this study highlight the efficacy of cerium oxide nanoparticles against bacterial pathogens that may be exploited for the development of new alternative antimicrobial agent.[33]

Liu *et al.* synthesised cerium nanostructures by green synthesis using tea extract for characterization and Adsorption of dye from aqueous phase. He collected the tea waste samples were dried at room temperature for 24 hours and stored in a thermostat. Five grams of tea waste was weighed and mixed with 100 mL of distilled water in a 250 mL beaker.[34] The mixed solution was treated with a 100 rpm for 60 min at 353 K. After cooling, the extract solution was centrifuged at 5000 rpm for 5 min and filtered . To prepare the cerium precursor, 0.05 mol cerium chloride was added to a 20 mL of extract solution and continuously stirred for 12 hours using a magnetic stirrer. After stirring, the gel-cerium precursor was formed and

dried at 393 K for 24 hours in an oven. The dried gel-cerium samples were calcined at different temperatures under air atmosphere. The obtained cerium nanostructures samples were characterized by thermogravimetric analyzer (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The cerium nanostructures were analyzed by using isotherm, kinetic investigations and adsorption evaluation for Congo Red (CR)[34].

Naseer *et al*. synthesised zinc nanoparticles by green synthesis using leaf extracts of *Cassia fistula* and Melia *azadarch* and their antibacterial potential. About 0.01 M zinc acetate dihydrate was used as a precursor in leaf extracts of respective plants for NPs synthesis. The structural and optical properties of NPs were investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), ultraviolet-visible spectrophotometer (UV-Vis) and dynamic light scattering (DLS). The antibacterial potential of ZnO NPs was examined by paper disc diffusion method against two clinical strains of *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) based on the zone of inhibition and minimal inhibitory indices (MIC) [35].

Ezcalisiji *et al.* synthesized zinc oxide nanoparticles (ZnO NPs) prepared via a precipitation method. Green synthesized ZnO NPs have a wide range of uses such as biomedical applications, water purification, optical devices and gas sensors. The non-toxic and economical technique described in this article is favorable for large-scale production too. ZnO NPs were produced from a zinc acetate precursor with dye extract of Ixora Coccinea (IC) leaves as a capping agent. The as-prepared ZnO NPs were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), UV-visible (UV-vis), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques. The XRD analysis showed an average crystallite size of 23 nm. The SEM analysis revealed a reduction in aggregation of ZnO crystallites due to addition of dye extracts of IC. EDX and UV-vis results confirmed the formation of pure ZnO NPs [36].

Kalantari *et al.* synthesis and evaluation of a polyvinyl alcohol/chitosan (PVA/chitosan) hydrogel incorporated with green synthesized cerium oxide nanoparticles (CeO_2-NPs) using a *Zingiber officinale* extract as the reducing, capping and stabilizer agent for wound healing applications. The PVA/chitosan/CeO_2-NPs hydrogel was synthesized via the freeze-thaw technique with 0 to 1% (wt) 5 nm CeO_2-NPs. Results revealed that the hydrogels containing 0.5% of CeO_2-NPs showed better antibacterial activities after just 12 hr (with MRSA but not *E.*

coli) and healthy human dermal fibroblast viabilities up to 5 days (more than 90%) compared to the control group. Therefore, these chitosan/PVA hydrogels incorporated with Ce-NPs could be a potential candidate as a robust wound dressing agent that impressively may decrease wound infections without resorting to the use of antibiotics[37].

 Bibi *et al.* [38].

 Akbari *et al.* synthesized through a green based sol–gel method from nitrate precursors and gelatin at the fixed calcination temperature of 600 °C maintained for 2 h. The powder X-ray diffraction (PXRD) patterns displayed the single-crystalline structure of these particular samples, which seemed to be completely indexed with the cubic fluorite phase. The evolution of crystalline phases in $Ce_{1-x}Zn_xO_2$ are assured by the observed broadening in PXRD peaks, while the field emission scanning electron microscopy (FE-SEM) images revealed that the spherical-shaped single-crystalline NPs do exist and confirmed the size estimations that were obtained from the Scherrer's equation. A dose dependent toxicity with non-toxic effects of concentrations up to 31.25 μg/ml is illustrated through the *In vitro* cytotoxicity studies regarding Neuro2A cells. [39].

CHAPTER 3

CHARACTERIZATION TECHNIQUES

3.0 Introduction

Nanoscience and nanotechnology are considered to be the key technologies for the current century. The fundamental of nanotechnology lies in the fact that size is reduced to the nanometer range. But measuring this nano dimension is not a very easy task. Although research is going on to synthesize nanostructured and nanophasic materials, characterizing these nano sized materials is now an established field. Thus, nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated nano characterization technique to allow a better control of structural analysis, morphology, properties, size and dimensions of a materials in nano range [40].

3.1. X-Ray Diffraction (XRD)

X-ray diffraction is a powerful tool for materials characterization. Typically, XRD provides information regarding the crystalline structure, nature of the phase, lattice parameters and crystalline grain size. The latter parameter is estimated by using the Scherrer equation using the broadening of the most intense peak of an XRD measurement for a specific sample. The Scherrer equation can be written as:

$$D = k\lambda/\beta cos\theta \quad \text{...} \textbf{(1)}$$

Where:

K is a dimensionless shape factor with a value close to unity, λ is the X-ray wavelength and θ is the Bragg angle.

3.1.1 Principle

The materials are made of using atoms and those are systematically arranged into a crystal structure. When the X-ray beams are fall on the surface of a crystal plane (sample) with an angle called glancing angle (θ). The X-ray beams are reflected from the atomic plane, called as a diffracted beam. If the reflected X-ray wave undergoes constructive interference, they are said to be diffracted by the crystal plane [41]. The intensity of diffracted X-ray beam is the function of incident angle 2θ and it produces diffraction pattern [42].

$$n\lambda = 2d\ sin\theta...(2)$$

Where:

n = integer

λ = wavelength of X-ray radiation

d = spacing between the set of crystal planes

θ = glancing angle between the radiation and surfaces

The X-ray diffraction can be interpreted by Bragg's law and it can be understood by the following Fig 3.1
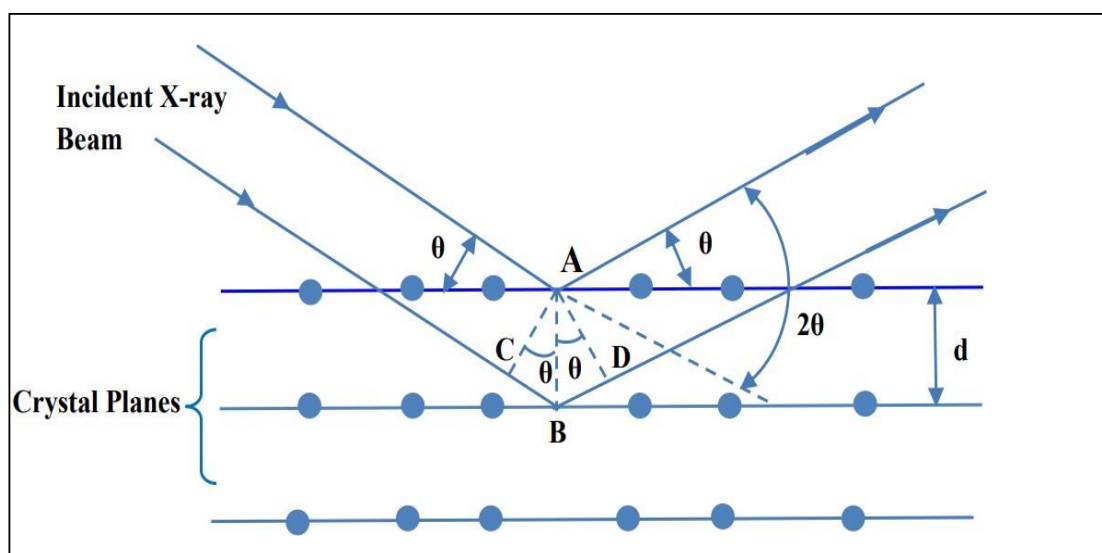

Figure 3.1 Diffraction of X-rays from the crystal plane.

In the above diagram the incident X-Rays have fixed values of wavelength and inter planar distance d is constant. The diffraction occurs at several angles of incidence such as θ1, θ2, θ3,.. corresponding to n = 1, 2, 3,..the order of reflection. If the difference between their path lengths is zero or an integer multiple of wavelength then these two waves are completely in phase and constructive interference pattern occurs. When the difference between the two rays is λ/2 then these two waves are out of phase and destructive interference pattern occurs [43]. The crystal structure of any substance scatters X-ray wavelength in its own unique diffraction pattern is also called as fingerprint of its atomic and molecular structure [41].

3.1.2 Instrumentation

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector.

Figure 3.2 Bruker's X-ray Diffraction

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with Cu K_α radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.
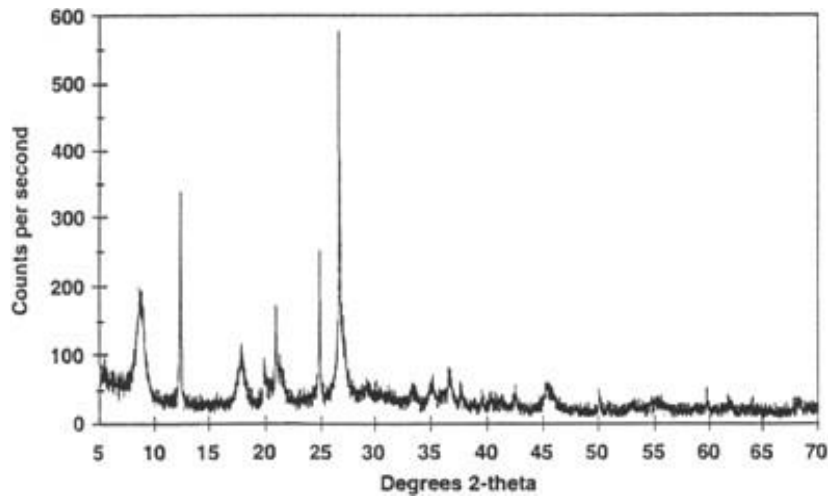
Figure 3.3 Refinement technique in XRD

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are present in the X-ray scan [44].

3.1.3 Applications

o X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).
o Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.
o Characterization of crystalline materials
o Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
o Determination of unit cell dimensions
o Measurement of sample purity

3.1.4 Strengths

o Powerful and rapid (< 20 min) technique for identification of an unknown mineral
o In most cases, it provides an unambiguous mineral determination
o Minimal sample preparation is required
o XRD units are widely available

3.1.5 Limitations

o Homogeneous and single phase material is best for identification of an unknown

o Must have access to a standard reference file of inorganic compounds (d-spacings, hkls)

o Requires tenths of a gram of material which must be ground into a powder

o For mixed materials, detection limit is ~ 2% of sample [44].

3.2 UV-Visible Spectroscopy

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400nm) is absorbed by the molecule which results in the excitation of the electrons from the ground state to higher energy state.

Nanoparticles have optical properties that are sensitive to size, shape, concentration, agglomeration state, and refractive index near the nano particle surface, which makes UV/Vis/IR spectroscopy a valuable tool for identifying, characterizing, and studying these materials. Standard UV-Vis analysis is performed with an agilent 8453 single beam diode array spectrometer, which collects spectra from 200-1100 nm using a slit width 1nm. Deuterium and tungsten lamps are used to provide illumination across the ultra violet electromagnetic spectrum. Spectra are typically collected from 1ml of a sample dispersion, but we can tests volumes as small as 100microlitre using a microcell with a path length of 1cm.
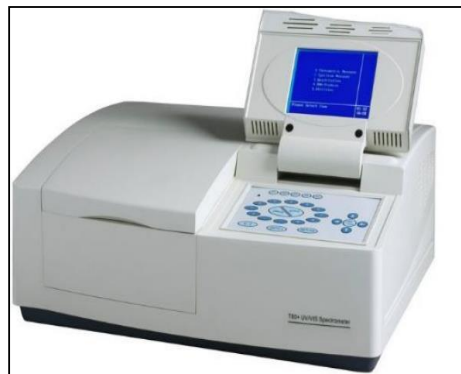

Figure 3.4 UV-VIS Spectrometer

3.2.1 Transmittance and Absorbance

The transmittance of a sample(T) is defined as the fraction of photons that pass through the sample over the incident number of photons, i.e.,

$$T = \frac{I}{I_0}$$

In a typical UV/Vis spectroscopy measurement, we are measuring those photons that are not absorbed or scattered by the sample. It is common to report the absorbance (A) of the sample, which is related to the transmittance by

$$A = -\log_{10}(T)$$

The relative percentage of scatter or absorption from the measured extinction spectrum depends on the size, shape, composition, and aggregation states of the sample. The sample may absorb light, scatter light, or both. As a general rule, smear particle will have a higher percentage of their extinction due to absorption.

3.2.2 Principle

Basically, spectroscopy is related to the interaction of light with matter. As light is absorbed by matter, the result is an increase in the energy content of the atoms or molecules. When ultraviolet radiations are absorbed, this results in the excitation of the electrons from the ground state towards a higher energy state. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light it can absorb. The absorption of ultraviolet light by a chemical compound will produce a distinct spectrum which aids in the identification of the compound.

3.2.3 Instrumentation
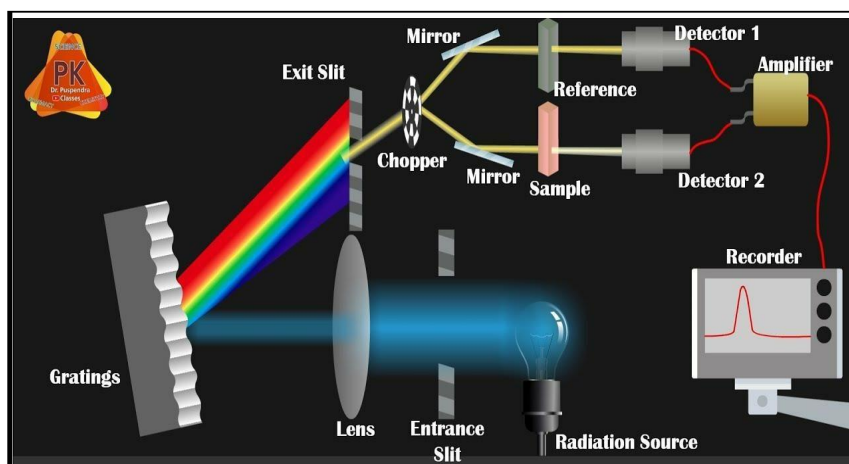

Figure 3.5 Working of U-V Spectroscopy

Light Source

Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red

radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

Monochromator

Monochromators generally is composed of prisms and slits. Most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results ina series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

Sample and reference cells

One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

Detector

Generally, two photocells serve the purpose of detector in UV spectroscopy. One of the photo-cell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Amplifier

The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servo-meter. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

Recording devices

Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

3.2.4Applications

o   It is one of the best methods for determination of impurities in organic molecules.

o   Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.

o   It is useful in the structure elucidation of organic molecules, such as in detecting the presence or absence of UNSATURATION, the presence of hetero atoms.

o UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation [45].

❖ **Tauc Plot Method**

The Tauc method of optical absorption edge determination as applied specifically to direct bandgap material. A misuse of the Tauc plot to determine the bandgap energy of semi-conductors may lead to erroneous estimates, particularly large errors can be associated with characterization of modified semi-conductors showing a significant absorption of sub bandgap energy photon. The bandgap energy of a semi-conductor describes the energy needed to excite an electron from the valence band to the conduction band. We determine the bandgap by plotting [(F(r) hv)2 vs hv] , where hv is the photon energy and F(r) is the (Kubelka-Munk) K-M function , thus extrapolating these regions we get the energy of the optical bandgap of the material.

So, with the help of DRS we calculate the bandgap with the help of K-M function.
$$(r) = k/s \qquad ,\ldots\ldots\ldots\ldots.(5)$$
where k is the molar absorption co-efficient, k= $(1-R)^2$, R is the Reflectance and S is the scattering factor, S=2R

The photon energy hv can be calculated using the equation,
$$hv = 1240/ wavelength \qquad \ldots\ldots\ldots\ldots.(6)$$
the Tauc method uses simple multi-wavelength absorption spectroscopy and is relied upon for material evaluation of functional photovoltaic layers, transparent conductors, sensor coatings and films used for many other applications [46].

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR instrument is one of the most important tools to identify the chemical components that are either organic (or) inorganic compounds presence in the synthesized materials. The FTIR analysis was used to find out the presence of various functional groups presence in the prepared sample which was taken in solid and liquid state using Perkin-Elmer spectrometer in the range of 400-4000 cm-1.

3.3.1 Physical Principles
Various frequencies, molecular bonds are vibrating owing to their elements and bonds presence in the synthesized material. According to the quantum mechanics, several specific frequencies were vibrating such as ground state at lowest frequency and several excited states

at higher frequencies. If the frequency of a molecular vibration linearly increases, the light energy will be absorbed, which may happen by the difference between two energy states (ground state (E_0) – first excited state (E_1)) and the relation is given below,

$$E_1 - E_0 = hc/\lambda \dotfill (3)$$

Where, h represents the Planck's constant, c denotes the velocity of the light and λ is the wavelength of light.

3.3.2 Experimental

The figure below shows the basic set up of the FTIR spectrometer. The FTIR spectrometer has following parameters such as (i) interferometer which consist of two mirrors such as infrared detector and beam splitter, (ii) detector, (iii) monochromator and (iv) chopper. In the FTIR studies, both solid and liquid samples were used to analysis. The KBr (or) polyethylene pellets were used to take the solid and liquid sample in FTIR analysis. For solid sample, few milligrams of the prepared samples are mixed with the KBr and fine grain in the mortar. After that the fine powder was pressed with the hydraulic pressure to make the pellet. Finally, the pellet sample was fixed with sample holder to take the FTIR analysis. For liquid sample, few drops of the samples were dropped into pure KBr pellet and few minutes dried the pellet at room temperature. After that the pellet was used to FTIR characterization.
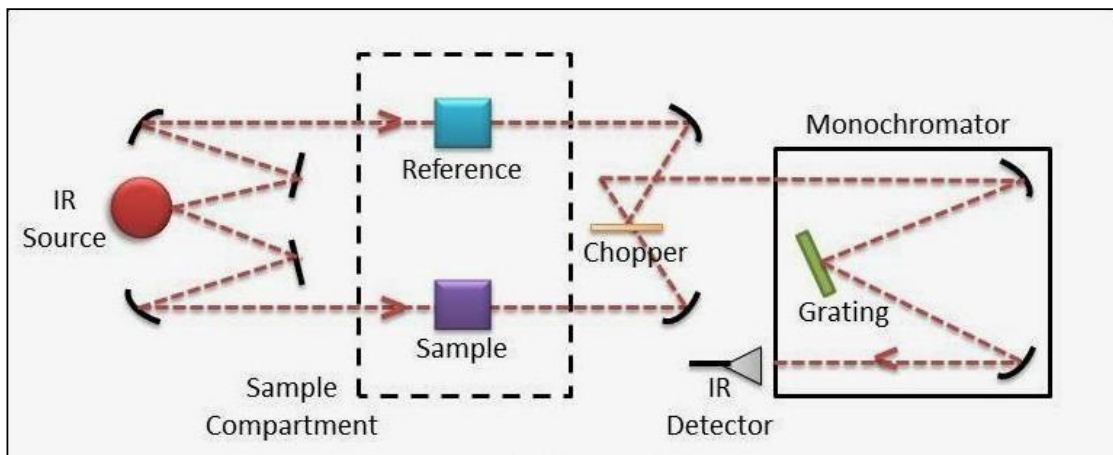

Figure 3.6 FTIR instrument setup

3.3.3 Applications

o Quality verification of incoming/outgoing materials
o Deformulation of polymers, rubbers, and other materials through thermogravimetric infra-red (TGA-IR) or gas chromatography infra-red (GC-IR) analysis

- o Microanalysis of small sections of materials to identify contaminants
- o Analysis of thin films and coatings
- o Monitoring of automotive or smokestack emissions
- o Failure analysis [47]

3.3.4 Strengths

- o Highly sensitive and quick method to achieve high quality spectrum.
- o This spectroscopy gives better signal to noise ratio compared to the dispersive instrument.
- o Gases, solids as well as liquid can be analysed with FTIR.
- o By using FTIR no external calibration is required and gives accurate results.
- o Organic compounds and Inorganic compounds can be identified easily using fourier transform infrared spectroscopy.
- o Simultaneous analysis can be done for multiple gaseous compounds.
- o FTIR can identify even small concentrations of contaminants.
- o FTIR has a laser beam which keeps the FTIR instrument accurately calibrated.
- o High resolution [48].

3.3.5 Limitations

- o The sampling chamber of an FTIR can present some limitations due to its relatively small size.
- o Mounted pieces can obstruct the IR beam. Usually, only small items as rings can be tested.

Several materials completely absorb Infrared radiation; consequently, it may be impossible to get a reliable result [49].

3.4 X-ray Photoelectron Spectroscopy (XPS)

When a sample is bombarded with monochromatic soft X-rays, the basic principle of XPS is that electrons are emitted from the sample surface. The kinetic energy of a released electron provides information on the binding energies of atomic orbitals, allowing surface chemical species to be identified. XPS (Figure.3.7) can be used to determine the relative concentration of species. The following relationship [50,51] can be used to calculate photon interactions with the core level.

$$KE = h\nu - BE - c\varphi$$

Where is the energy of an incident X-ray, and stands for the atomic orbital binding energy, stands for the spectrometer work function, and stands for the kinetic energy of the released electron. Each electron in an atomic orbital has its own unique binding energy. The electron kicked off from the innermost orbitals with their kinetic energy associated with the binding

energy of the atomic orbital due to the absorption of incoming X-rays. Information about the state of elements can then be obtained by analysing these energies. Peak intensity can provide quantitative information about an ingredient.

The following are the most commonly used monochromatic X-ray sources.

• hv = 1253.6 eV for $Mg\ K\alpha$ radiation

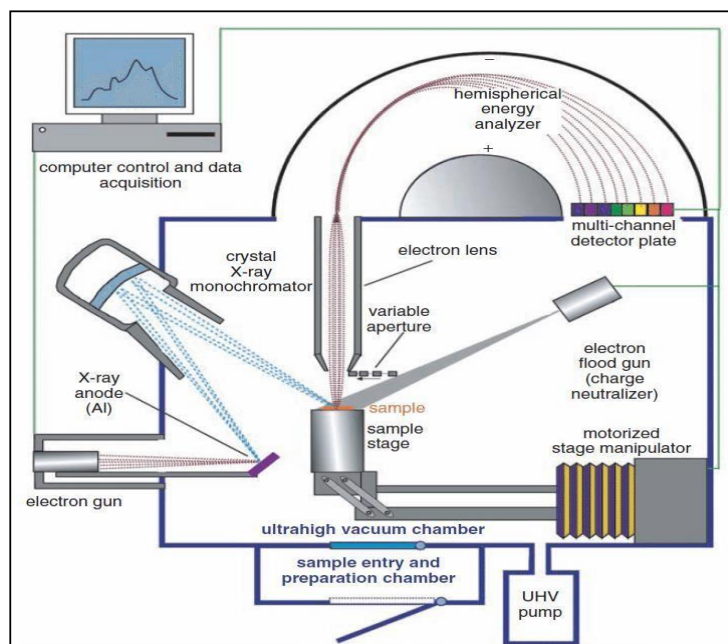• $Al\ K\alpha$ radiation has a wavelength of hv = 1486.6 eV.

Figure. 3.7 Schematic of XPS

The ejected electron can have an energy range of 0–1480 eV is excited by $Al\ K\alpha$ and $Mg\ K\alpha$ excites 0–1250 eV. Generally, due to the short inelastic mean free path of electrons this technique is very strong, it is very surface sensitive. The spectra were obtained on Thermo Scientific ESCALAB 250 Xi, using monochromatic Al Kα radiation (1486.6 eV). The obtained spectra were then analysed.

CHAPTER 4

MATERIALS AND METHODS

4.1 Experimental Methods

Magnesium Oxide, Zinc Oxide *Sauropus androgynous* Leaf extract, Distilled Water.

4.2 Materials Used

Cerium Nitrate Hexahydrate, Zinc Nitrate Hexahydrate, Magnisium Nitrate Hexahydrate, Distilled water and *Sauropus androgynous* Leaf extract.

4.2.1 Cerium Nanoparticles

Cerium is the most abundant rare earth alkali element which is listed in the F block of the periodic table, and they are found in minerls, namely synchysite, hydroxylbaxyl bastnasite, monozite, zircon, rhabdophane, sallanite and bastnasite. Cerium exhibits exceptional character of cycling between the two inonic states, which is Ce^{3+} and Ce^{4+}, and this is possible due to the presence of ground-state electron in the 4f orbital which enables it to exhibit redox properties. Further the cerium oxide nanoparticle (Ce_4O_8) is a face-centered (fcc) fluorite lattice comprising of eight oxygen atoms bonded to the cerium atom and the complete unit cell measures 5.1Å on an edge.The building blocks of nanoparticles are the crystalline nature of the particle, and in the cerium oxide nanoparticle, polycrystallinity is more common. It is a rare earth metal that combines with oxygen to produce cerium oxide nanoparticles with a crystalline structure. Cerium oxide nanoparticles exhibit excellent antioxidant characteristics because of the redox cycling between the two active states of cerium, 3+ and 4+. Due to a large number of oxygen-containing functional groups in CeO2 nanoparticles, they can operate as an electrolyte in supercapacitors, as well as in nanomaterial applications such as fuel cells, rust inhibitors, and catalytic converters. CeO_2 nanoparticles are used for a wide variety of applications in the healthcare industry as well. When tested against several types of bacteria, these rare earth nanoparticles (nanoceria) showed a significant antibacterial impact. In addition to their natural ability to change oxidation states, CeO2 nanoparticle can also protect healthy cells from oxidative damage. Furthermore, cerium oxide nanoparticles can function as synthetic oxidative electrocatalysts with observable central nervous system (CNS) penetrance, sustained preservation, and restorative catalytic properties. Cerium Oxide belongs to semiconductor nanoparticle.

Applications of Cerium Oxide nanoparticle

Cerium Oxide ,also called Ceria ,is widely applied in glass, ceramics and catalyst manufacturing .In glass industry,it is considered to be the most efficient glass polishing agent for precision optical polising.It is also used to decolorize glass by keeping iron in its ferrous state.The ability of Cerium-doped glass to block out ultra violet light is utilized in the maufacturing of medical glassware and aerospace windows.It is also used to prevent polymers from darkening in sunlight and to suppress discoloration of television glass.It is applied to optical components to improve perfomance.High purity Ceria are also used in phosphors and dopant to crystal.

Biosafety concerns Cerium Oxide nanoparticle

Continuous, frequent use of these nanomaterials has resulted in their constant discharge into the atmosphere, where human exposure can cause severe health issues. Therefore, toxicity and biosafety evaluation are crucial before their widespread use in industrial applications increases. On the other hand, harmful consequences of cerium oxide nanoparticles have also been described, including cell death. Harmful impacts were shown to be due to the formation of reactive oxygen species (ROS), which can induce cellular damage and eventually result in the initiation of cell death. Interestingly, it has also been shown that cerium oxide nanoparticles display either antioxidant or pro-oxidative characteristics[23].

4.2.2 Sauropus androgynus (L.) Merr.

Sauropus androgynus, also known as sweet leaf, is a shrub grown in some tropical regions as a leaf vegetable. In Kerala, it is called mysore cheera. Its multiple upright stems can reach 2.5 meters high and bear dark green oval leaves 5–6 cm long. It is a good source of vitamin K. It also has high level of provitamin A carotenoids, especially in freshly picked leaves, as well as high levels of vitamins B and C, protein and minerals.

It is common in evergreen forest. The leaves of this plant have been traditionally used to treat certain diseases, for weight loss, and as vegetable dishes. SA leaves contain an adequate number of macronutrients and having most of the micronutrients. The more the leaves mature, the higher the nutrient content of the leaves.

SA leaves also contain most of the essential minerals, including sodium, potassium, calcium, phosphorus, iron, magnesium, copper, zinc, manganese, and cobalt. Fresh leaves of SA typically consist of 70%-90% moisture, 3%-8% protein, 1%-4% fat, 1%-2% fiber, and about 2% ash. The other percentage of the leaves is carbohydrate. SA leaves are the staple food in some of the developing nations that provide essential nutrients to the poor people. It also helps to maintain good health of these people. However, fresh consumption and over-consumption of SA leaves are not advisable

4.3 Synthesis Procedure

4.3.1 Green Synthesis

Nanoparticles made by green technology are far superior to those manufactured with physical and chemical methods based on various aspects. For example, green techniques eliminate the use of expensive chemicals, consume less energy, and generate environmentally benign products and by products.Green synthesis of nanoparticles involves the use of plant or plant parts for. the bioreduction of metal ions into their elemental form in the size range 1–100 nm. The process of green synthesis is more efficient, simpler, and economical, and can easily be scaled up to perform larger operations.
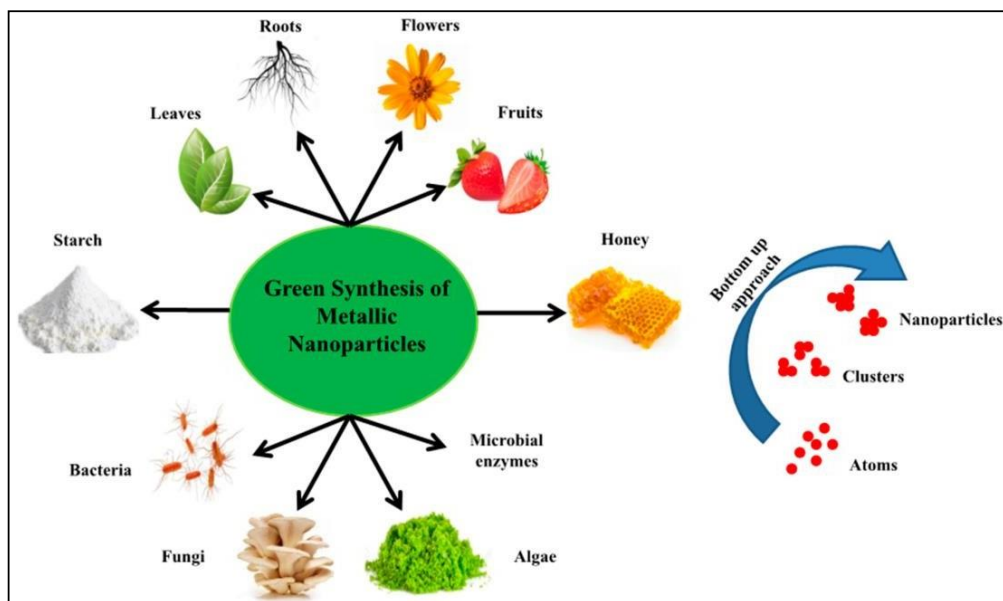

Figure 4.1 Green synthesis of Metallic nanoparticles

Preparation of leaf extract

50g of fresh leaves of Sauropus androgynus (mysore cheera) were washed thoroughly with plenty of distilled water and both surface of leaves was sterilized using alcohol by gently rubbing. These leaves were kept in a wire gauss and heated for 30min in 100ml of distilled water at 75 degree celsius. Then the extract was filtered two times using Whatman filter paper no.1. The final filtrate was stored in cool dry place for further use.

Figure 4.2 Leaf extract

<u>Preparation of cerium nitrate hexahydrate</u>

About 2.1711g of cerium nitrate hexahydrate was added to 100ml double distilled water to get 0.1M solution. The mixture was stirred using a magnetic stirrer for 10min to get a homogeneous solution.

Figure 4.3 Preparation of Cerium nitrate hexahydrate

<u>Green synthesis of cerium oxide nanoparticles</u>

100ml of the cerium nitrate hexahydrate of 0.1M solution was heated at 50 degree celsius for 10min and 50ml of leaf extract was added drop wise to it under stirring by using magnetic stirrer for 180 min.The reaction mixture became yellowish and cream coloured precipitate of cerium hydroxide was left for 3min for complete reduction to cerium hydroxide. Then the precipitate was filtered using Whatman filter paper no.1. The precipitate was dried using infrared lamp and the sample was stored for further studies.

4.4 <u>Zinc Oxide</u>

Zinc oxide of considered to be a technologically prodigious material having a wide spectrum of applications such as that of semiconductor , magnetic material, nanostructure varistor, thermo electric material , gas sensor, constituent of cosmetics etc.There are several synthesis procedures for the preparation of ultraline oxide nanoparticles such as sol-gel, spray pyrolysis,

chemical vapour deposition, precipitation method, hydrothermal process for the method for the preparation of ZnO material. Planted mediated synthesis of nanoparticles is a revolutionary technique that has wide range of application in agriculture , food industry and medicine. Due to physio- chemical properties of plant base nanoparticles, this method also offer an added advantage of increased life span of nanoparticles.

4.4.1 Synthesis Procedure

Preparation of leaf extract

50g of fresh leaves of Sauropus androgynus (mysore cheera) were washed thoroughly with plenty of distilled water and both surface of leaves were sterilized using alcohol by gently rubbing. These leaves were kept in a wire gauss and heated for 30min in 100ml of distilled water at 75 degree celsius. Then the extract was filtered two times using Whatman filter paper no.1. The final filtrate was stored in cool dry place for further use.

Preparation of Zinc doped cerium nanoparticles

About 2 percentage of zinc nitrate hexahydrate doped with 2.1711g of cerium nitrate hexahydrate was added to 100ml double distilled water to get 0.1M solution. The mixture was stirred using a magnetic stirrer for 10min to get a homogeneous solution.

Green synthesis of zinc doped cerium nanoparticles

100ml of the cerium nitrate hexahydrate of 0.1M solution was heated at 50 degree celsius for 10min and 50ml of leaf extract was added drop wise to it under stirring by using magnetic stirrer for 180 min.The reaction mixture became yellowish and cream coloured precipitate of cerium hydroxide was left for 3min for complete reduction to cerium hydroxide. Then the precipitate was filtered using Whatman filter paper no.1. The precipitate was dried using infrared lamp and the sample was stored for further studies.

4.5 Magnesium Oxide

 Magnesium oxide is an inorganic salt of magnesium formed with ions of magnesium formed with ions of magnesium and oxygen.It's one of many forms of magnesium available for purchase in supplement form. It is added to dietary supplements as well as over the counter medications used to treat indigestion and headaches. Magnesium oxide nanoparticles are odorless and non-toxic.They possess high hardness, high purity and a high melting point. Planted mediated synthesis of nanoparticles is a revolutionary technique that has wide range of application in agriculture, food industry and medicine. Due to physio- chemical properties

of plant base nanoparticles, this method also offers an added advantage of increased life span of nanoparticles.

Preparation of leaf extract

50g of fresh leaves of Sauropus androgynus (mysore cheera) were washed thoroughly with plenty of distilled water and both surface of leaves were sterilized using alcohol by gently rubbing. These leaves were kept in a wire gauss and heated for 30min in 100ml of distilled water at 75 degree celsius. Then the extract was filtered two times using Whatman filter paper no.1. The final filtrate was stored in cool dry place for further use.

Preparation of Magnesium doped cerium nanoparticles

About 2 percentage of zinc nitrate hexahydrate doped with 2.1711g of cerium nitrate hexahydrate was added to 100ml double distilled water to get 0.1M solution. The mixture was stirred using a magnetic stirrer for 10min to get a homogeneous solution.

CHAPTER 5

RESULT AND DISCUSSION

5.1 X-ray Diffraction Analysis

XRD spectrum of CeO2 nanoparticles synthesized at 180°C in 2θ range of 30° to 80° using CuKα radiation (λ = 0.1504nm) were shown in the figure. The sample shows diffraction peaks at 2theta= 28.62°,47.71°,56.23°,88.27 corresponding to the crystal plane (111),(200),(220),(221) which attributes to face centered cubic structure (fcc) of CeO_2 nanoparticles. The comparatively intense peak refers a moderate crystalline size. The average crystalline size(D) of CeO_2 nanoparticles are calculated by the Debye-Scherer equation,

$$D= \frac{k\lambda}{\beta \cos \theta}$$

λ is the wavelength of the Cu-kα radiation, ,D is the crystalline size, k is a constant and its value is taken as 0.9, θ is the diffraction angle and β is the full-width half maximum(FWHM).The average crystalline size is 2.7577nm for CeO_2 nanoparticles .
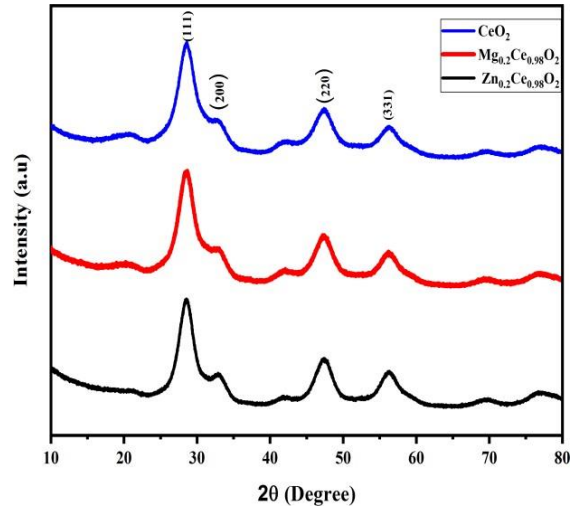

Figure 5.1 XRD spectra of Cerium oxide , Zinc doped Cerium oxide, Magnesium doped Cerium oxide nanoparticles
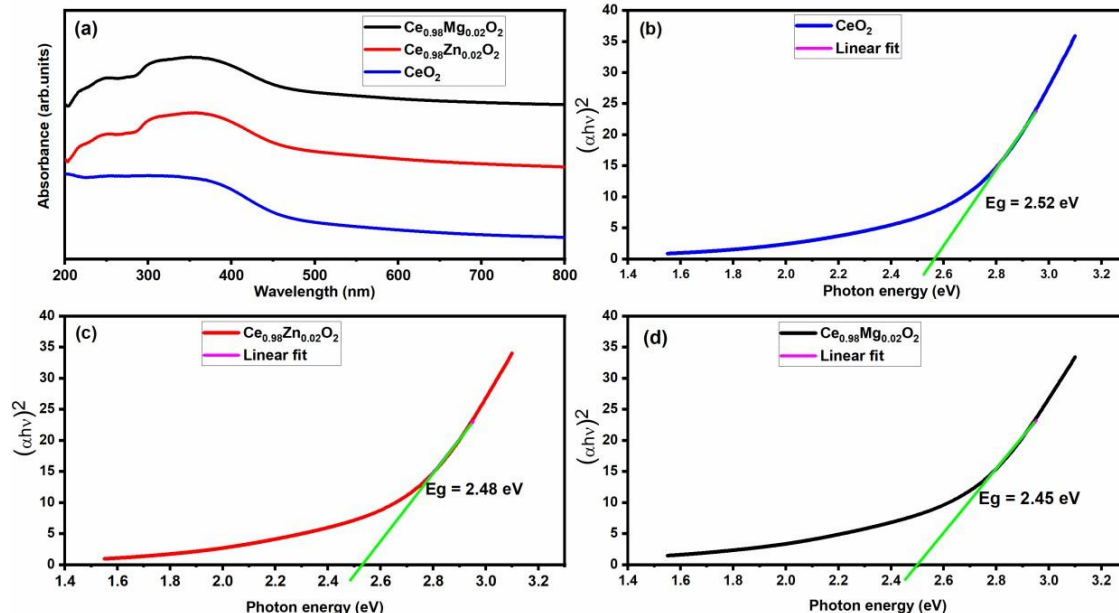
5.2 UV-Visible Spectroscopy

Figure 5.2 (a)UV-Visible reflectance spectrum of cerium oxide (b) Tauc's plot of cerium oxide nanoparticles.(c) Tauc's plot of Zinc doped Cerium nanoparticles (d) Tauc's plot of Magnesium doped Cerium nanoparticles

Optical properties of green synthesized Cerium oxide, Zinc doped Cerium oxide, Magnesium doped Cerium oxide nanoparticles were studied using Jasco V 760 spectrophotometer. The above figures show UV-Visible reflectance spectrum of the sample recorded in the range of 200-800nm.

5.2.1 Determination of Optical band gap-"Tauc's plot"

One of the most important parameter deals with the material properties is their bandgap. By Diffuse Reflectance Spectrum the bandgap Eg was found by Tauc plot method by calculating Kubelka-Munk function.The optical bandgap of synthesized Cerium oxide, Zinc doped cerium oxide, Magnesium doped cerium oxide nanoparticles were estimated by the shoulder peak of the spectra corresponds to fundamental absorption edges in the samples.The absorption of samples were verified by using Kubelka-Munk (K-M) function is given by,

$$\alpha \approx \frac{k}{s} = \frac{(1-R_\infty)^2}{2R_\infty}$$

where R, k and s are reflection, absorption and scattering coefficient. Tauc's plot equation

$$\alpha h\nu = \beta\left(h\nu - E_g\right)^n$$

where c is a constant independent of energy , h is Plank's constant, v is the frequency of the incident photon ,Eg is the optical bandgap energy of the nanomaterial and 'n' is the power factor .It is the clear from the above equation that the fundamental energy band gap depends on variation in optical absorption coffecient.Depending upon the nature of the transition n can have 1/2,3/2,2 or 3 direct aloowed,direct forbidden,indirect allowed,and indirect forbidden transition.The band gap energy of synthesized nanoparticles can extrapoliated linear fit for the plotted experimental data versus photon energy as shown in figure 5.2. Cerium oxide is a n-type semiconductor with wide band gap of range (2.6 to 3.4eV), depending on the preparation method. The bandgap value,Eg calculated from Tauc's plots are found to be 2.52,2.48 and 2.45eVs.The increase in band gap occurs, when the size of confinement of electrons and holes are compared with the reported papers

5.3 FTIR Analysis

To confirm the functionalization of CeO2 and doped samples the FTIR spectra of samples were recorded and are represented in Figure 2. In the FTIR spectrum of CeO2 sample, the peak at 3273 cm−1 corresponds to –OH stretching vibrations of the hydroxyl groups, while in the modified samples also , the —OH stretching is observed, which appears around the same frequency (3200–3600 cm−1). The band at 1636 cm−1 can be attributed to the interlayer stretching and bending vibration of molecular water. . The absorption band at about 533 cm−1 presented in both samples is representative of Ce–O stretching vibration. A strong band at ∼992 cm-1 is attributed to C-C bending vibration [50-51].
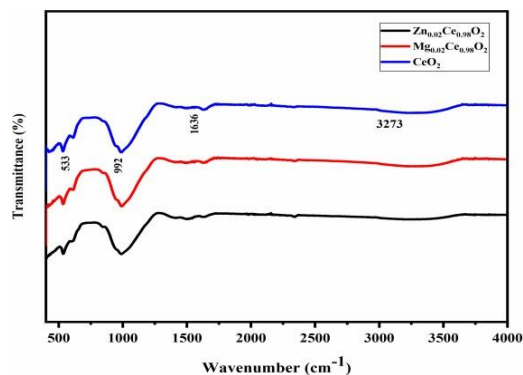

Figure 5.1 FTIR spectra of Cerium oxide , Magnesium doped Cerium oxide , Zinc doped Cerium oxide nanoparticle

5.4 X-ray Photoelectron Spectroscopy Analysis

XPS analysis was conducted to distinguish between the oxidation states of Cerium oxide and elements present Zn doped and mg doped in the cerium oxide nanoparticles. Figure 5.4 depicts a Ce 3d spectrum taken from the CeO_2. The Ce 3d spectrum exhibits Ce 3d5/2 and Ce 3d3/2

spin-orbit doublet peaks, respectively, at 882.1 and 899.9 eV. The strong satellite peaks locating at around 885.7 eV and 903.8 eV are due to the Ce3+ bonding of Ce_2O_3. These findings agree well with the data reported in the literatures. This validates that in the prepared cerium oxides nanoparticles contain non-negligible amounts of Ce 3+ were confirmed.

The Core level spectra Figure 5.5 of pristine and doped samples are also given in the spectra. From the spectra we can identify the elements which exhibit in the prepared samples. In the core level spectra of cerium oxide the existence Ce and O elements are observed also the doublets peak Corresponding for $Ce3d_{5/2}$ and $Ce3d_{3/2}$ are validating the confirmation of +3 oxidation state of cerium. In the core level spectra of mg doped Cerium oxide the presence of Mg, Ce and O are observed. This validates the successful doping of the Mg in cerium oxide. Zn doped Cerium spectra contains the presence of Z, Ce and O in core level spectra. So we can conclude that from the analysis it is confirmed that the successful doping of Zn and Mg into the CeO_2.
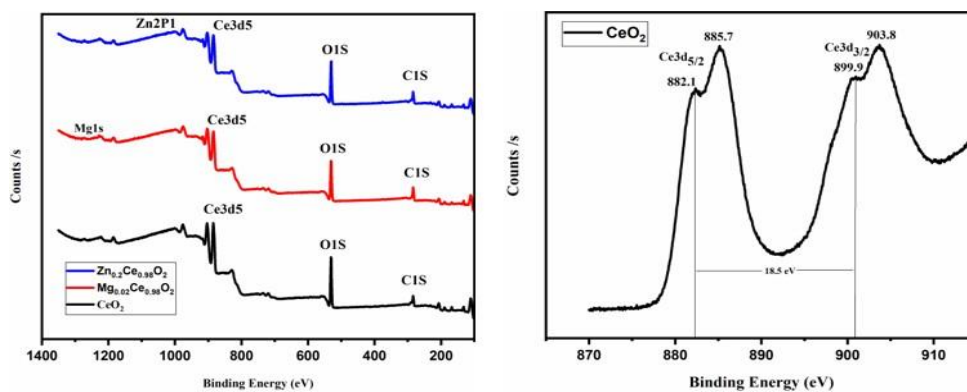

Figure 5.4 Corelevel spectra of prepared samples and Figure 5.5: Ce3d spectra of CeO_2

CHAPTER 6

CONCLUSION AND FUTURE SCOPE

6.1 <u>Conclusion</u>

It is important to need an environment friendly method to synthesis nanoparticles ,so I choosed green synthesis for the synthesis of nanoparticles. A simple, rapid biological procedure has been developed to synthesis cerium oxide nanoparticles with both valuable optical properties and biological properties directed by particle size using varying concentration of Sauropus androgynus (L.) Merr. leaf extracted solution. Also I doped 2% of zinc nitate hexahydrate and magnesium nitrate hexahydrate seperately into the cerium nitrate hexahydrate. The cerium oxide nanoparticles shows a crystalline size about 2.757nm. The various characterizations like FTIR, XRD, UV-Vis, EDX are studied. The explored, ecofriendly,high efficient cerium oxide nanoparticles prepared from Sauropus androgynus leaft extract are expected to have more extensive application in biomedical fields.

6.2 <u>Future Scope</u>

☐ Morphology dependent study can be done by changing different synthesizing

methods, precoursors and conditions etc

☐ Different dopants can be used for doping instead Zn and Mg inorder to tune the

properties

☐ We can make ternary,binary composites for the enhancement of properties

☐ Different applications can be done includes Photocatalysis, supercapacitors,

antibacterial, anticancerous studies etc

☐ Nonlinear and luminescence study can be done

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