GREEN SYNTHESIS OF PURE AND MAGNESIUM DOPED CERIUM OXIDE NANOPARTICLES

Dissertation submitted to University of Kerala in partial fulfilment of the requirements for the award of the degree of

Bachelor of Science in Physics

By

ARYA DEV V.A (Reg. No.: 23019101006)
ASHISH G ABRAHAM (Reg. No.: 23019101007)
GOPIKA S (Reg. No.:23019101028)

Bishop Moore College Mavelikara

Alappuzha – 690110

Kerala, India

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Department of Physics
Bishop Moore College Mavelikara

Signature of Examiners: Date:

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Certificate

This is to certify that the work presented in this dissertation entitled ***"Green Synthesis of Pure and Magnesium Dopped Cerium Oxide Nanoparticles "*** by **Arya Dev V.A. (Reg No. 23019101006)**, **Ashish G Abraham. (Reg No. 23019101007), Gopika S. (Reg No. 23019101028)** is a record of original research carried out by us under the guidance of **Dr. Jerin Susan John**, **Assistant Professor, Department of Physics, Bishop Moore College, Mavelikara**, Assistant Professor, Department of physics, Bishop Moore College, Mavelikara in partial fulfillment of the requirements of the bachelor of Science in Physics during the academic year 2019-2022. The dissertation represents an independent work from the part of the candidate.

Dr. D. Sajan   Dr. Jerin Susan John

Declaration

We hereby state that the dissertation entitled ***“Green Synthesis of Pure and Magnesium Dopped Cerium Oxide ”***submitted during our period of study for the award of Degree of Bachelor of Science in Physics is an authentic work carried out by us under the guidance of **Dr. Jerin Susan John**, **Assistant Professor, Department of Physics, Bishop Moore College, Mavelikara** ,Bishop Moore College,Mavelikara.. We also declare that the report is prepared only for our academic requirement not for any other purpose

Arya Dev V.A
Ashish G Abraham
Gopika S

Acknowledgement

We are happy to present this dissertation as a part of our Bachelor of Science programme. At this outset, we would like to express our gratitude to various people who have helped us at different stages of this work. Paramount among these, I thank God Almighty being with us every time.

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Arya Dev A

Ashish G Abraham

Gopika S

ABSTRACT

The study focuses on the fabrication of Cerium oxide (CeO_2) nanoparticle through green synthesis using S*auropus androgynus* leaf extract. Green synthesis method was proposed for the synthesis because it does not involve toxic chemicals and extreme environmental conditions which may be hazard in their field of application especially in the medical field. The nanoparticles can be produced inexpensively, safely and can be prepared easily. Characterization of the prepared samples were done using X-ray powder diffraction (XRD) and UV-Vis spectroscopic studies. The XRD pattern confirmed the cubic structure of CeO_2. The average crystalline size was estimated using the Scherrer equation and Williamson-Hall analysis. The crystalline size of the pure cerium oxide and magnesium doped cerium oxide obtained from the Scherrer method is 29.28nm and 35.055nm respectively while that from Williamson-Hall effect analysis is 23.77nmand 30.45nm respectively. Optical characterization of the CeO_2 nanoparticles was carried out by UV-Visible spectroscopy and obtained a reflectance peak around 370 nm for pure cerium and 367nm for magnesium doped cerium. The optical bandgap of the pure CeO_2 nanoparticles calculated form the Tauc plot found to be 3.28eV and that for the Mg-doped CeO_2 nanoparticles is 3.37eV.

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Chapter 1

INTRODUCTION

1.1 Nanotechnology

Nanotechnology, also shortened to nanotech, is the use of matter on an atomic, molecular, and supramolecular scale for industrial purposes[1][2]. A more generalised description of nanotechnology was subsequently established by the National Nanotechnology Initiative, which defined nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometers. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in nanomedicine, nanoelectronics, biomaterials energy production, and consumer products. Nanotechnology has received a lot of attention because they are accepted to be used in a variety of applications based on their excellent and unique visual, electrical, magnetic, biological or mechanical properties. Such properties come from well-designed nanoarchitectures and nanostructures of these materials. It has the potential to change our standard of living.[3]

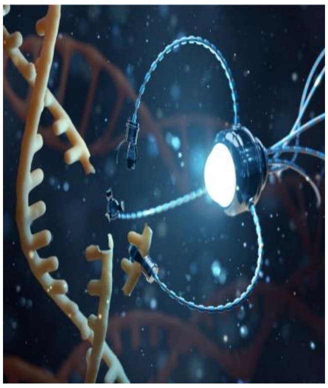

Figure 1.1 Nanotechnology in medicine

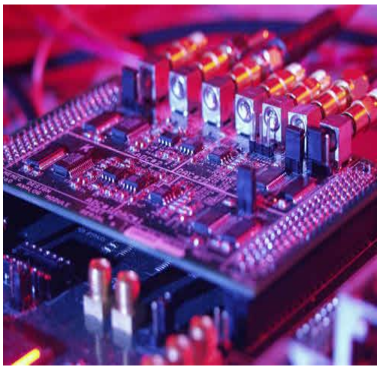

Figure 1.2 Nanotechnology in electronics

1.2 Origin of Nanotechnology

The concepts that seeded nanotechnology were first discussed in 1959 by renowned Physicist *Richard Feynman* in his talk *There is plenty of room at the Bottom*, in which he described the possibility of synthesis via direct manipulation of atoms. The term “nano-technology” was first used by *Norio Taniguchi* in 1974, though it was not widely known. Inspired by Feynman’s concepts, *K .Eric Drexler* used the term “nanotechnology”, which proposed the idea of a nanoscale “assemble” which would be able to build a copy of itself and of other items of arbitrary complexity with atomic control. Also in 1986, Drexler co-founded *The Foresight*

Institute to help increase public awareness and understanding of nanotechnology concepts and implications.[4]

1.3 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. [5]

Being much smaller than the wavelength of visible light (400-700nm), nanoparticles cannot be seen with ordinary optical microscopes, requiring the use of electron microscopes or microscopes with laser. For the same reason, dispersion of nanoparticles in transparent media can be transparent, whereas suspensions of larger particles usually scatter some or all visible light incident on them. Nanoparticle also easily pass through common filters, such as common ceramic candles, so that separation from liquids requires special nanofiltration techniques[6].

Nanoparticle occur widely in nature and are objects of study in many sciences such as *chemistry, physics, geology* and *biology.* Being at the transition between bulk materials and atomic or molecular structures, they often exhibit phenomena that are not observed at either scale. They are an important component of atmospheric pollution, and key ingredients in many industrialized products such as *paints, plastics, metals, ceramics and magnetic* products. The production of nanoparticle with specific properties is branch of Nanotechnology.[7]

1.4 Classification of nanoparticles

Nanoparticles can be classified into different types according to the size, morphology, physical and chemical properties. Some of them are carbon-based nanoparticles, ceramic nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles and lipid-based nanoparticles.

1.4.1 Carbon-Based nanoparticles

Carbon-based nanoparticles include two main materials: carbon nanotubes (CNTs) and fullerenes. CNTs are nothing but graphene sheets rolled into a tube. These materials are mainly used for the structural reinforcement as they are 100 times stronger than steel.

1.4.2 Ceramic nanoparticles

Ceramic nanoparticles are inorganic solids made up of oxides, carbides, carbonates and phosphates. These nanoparticles have high heat resistance and chemical inertness. They have applications in photocatalysis, photodegradation of dyes, drug delivery, and imaging..

1.4.3 Metal nanoparticles

Metal nanoparticles are prepared from metal precursors. These nanoparticles can be synthesized by chemical, electrochemical, or photochemical methods. In chemical methods, the metal nanoparticles are obtained by reducing the metal-ion precursors in solution by chemical reducing agents. These have the ability to adsorb small molecules and have high surface energy.

1.4.4 Semiconductor nanoparticles

Semiconductor nanoparticles have properties like those of metals and non-metals. They are found in the periodic table in groups II-VI, III-V or IV-VI. These particles have wide bandgaps, which on tuning shows different properties. They are used in photocatalysis ,electronic devices ,photo-optics and water splitting applications.

1.4.5 Polymeric nanoparticles

Polymeric nanoparticles are organic based nanoparticles. Depending upon the method of preparation, these have structures shaped like nanocapsular or nanospheres. A nanosphere particle has a matrix-like structure whereas the nanocapsular particle has core-shell morphology. In the former, the active compounds and the polymer are uniformly dispersed whereas in the latter the active compounds are confined and surrounded by a polymer shell.

1.4.6 Lipid-based nanoparticles

Lipid-based nanoparticles are generally spherical in shape with a diameter ranging from 10 to 100nm. It consists of a solid core made of lipid and a matrix containing soluble lipophilic molecules. The external core of these nanoparticles is stabilized by surfactants and emulsifiers. These nanoparticles have application in the biomedical field as a drug carrier and delivery and RNA release in cancer therapy.[8]

1.5 Applications of nanoparticles

1.5.1 In materials

- Polymers

- Food packaging
- Flame retards
- Light control

1.5.2 In medicine

- Effective for drug delivery
- Delivery of medicine to the body

1.5.3 In agriculture

- Nanoformulations of agrochemicals for applying pesticides and fertilizers for crop improvement.
- The application of nanosensors in crop protection for the identification of diseases and residues of agrochemicals.
- Nanodevices.

1.5.4 In environment

- Wastewater treatment.
- Removal of hazardous pollutants.
- Emission control technologies.
- Corrosion protection from the automotive industry.

1.6 Synthesis methods

In the synthesis of nanoparticle, which can be natural or synthetic origin and exhibit unique properties at the nanoscale, to basic approaches that include various preparation methods and are known from early times are used.

The first approach is the “top-down” method which calls for breaking down of solid materials into small pieces by applying external force. In this approach, many physical, chemical and thermal techniques are used to provide the necessary energy for nanoparticle formation. The second approach, known as “bottom-up” is based on gathering and combining gas or liquid atoms or molecules. These two approaches have advantages and disadvantages relative to each other. In the up-down approach, which is costlier to implement, it is impossible to obtain perfect surfaces and edges due to cavities and roughness that occur in nanoparticles; whereas excellent nanoparticle synthesis results can be obtained by bottom-up approach. In addition, with the bottom up approach, no waste materials that need to be removed are formed,and nanoparticles having smaller sizes can be obtained thanks to the better control of sizes of the nanoparticles.[9]

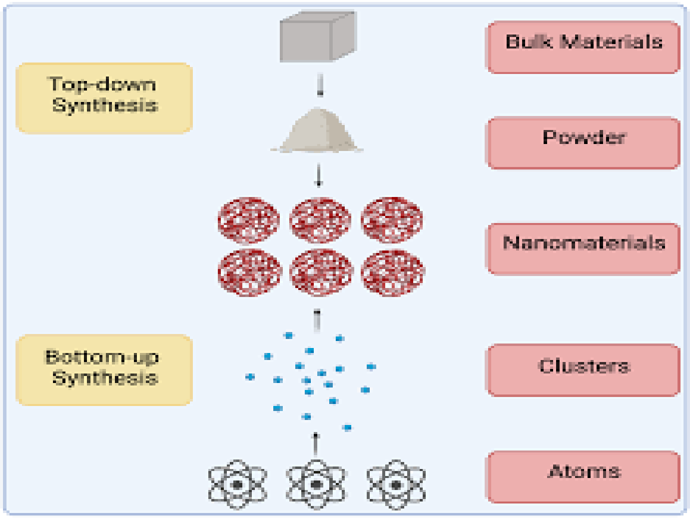

Figure 1.3 Synthesis approaches of naoparticle

1.6.1 Physical methods for the synthesis of nanoparticle

- Inert gas condensation
- Arc discharge
- RF-plasma
- Plasma arc technique
- Ion sputtering
- Laser ablation
- Laser pyrolysis
- Ball Milling
- Molecular beam epitaxy
- Chemical vapour deposition method

1.6.2 Chemical Methods for the synthesis of nanoparticle

- Solvothermal synthesis
- Aerosol based process
- Sol-gel
- Atomic or molecular Condensation
- Hydrothermal synthesis
- Cryochemical synthesis
- Spray drying

1.6.3 Biological Method for the synthesis of nanoparticle

- Nanoparticle synthesis by plant extract
- Nanoparticle synthesis by Bacteria
- Nanaoparticle synthesis by Fungi
- Nanaoparticle synthesis by Yeast
- Nanaoparticle synthesis by Biological particles[10]

1.7 Green synthesis method

The biological method, which is represented as an alternative method to chemical and physical methods, provides an environmental friendly way of synthesizing nanoparticles. This method employs an environmentally friendly process of constructing nanoparticle. Microorganisms such as bacteria, yeast, fungi, algal species and certain plants act as substrates for the green synthesis of nanomaterials. Moreover this methods, doesnot require expensive, harmful, and toxic chemicals.

Green synthesis of nanoparticlehas gained admirable traction in nanotechnology research.This approach which utilizes processes such as regulation, control, clean-up and remediation aims to increase the eco-friendly of these essential particles. By reducing harmful by-products produced through the process of conventional nanoparticle synthesis, there will be less toxic unsustainable products created.The use of natural resources such as organic systems will aid in achieving the goal of creating a greener and more sustainable economy;however, it will require industrial assistance with the adoption of these alternative approaches.[11]

1.7.1 Green synthesis using plant extract mechanism:

- A plant extracts is add to a metal solution.
- This mixture is stirred and observed the colour change.
- A colour change indicates the formation of nanoparticles in colloidal form.

1.7.2 Advantages of green synthesis

- Environmental friendly.
- Easily scaled up for large synthesis of nanoparticles.
- No need of high temperature, pressure, energy and toxic chemicals.
- More advantages over use of micro-organisms by less elaborate process of maintaining cultures.

- Reduces cost of micro-organisms isolation and their culture media.

1.7.3 Disadvantages of green synthesis

- Plants cannot be manipulated as the choice of nanoparticles through optimized synthesis through genetic engineering.
- Plant produce low yield of secreted proteins which decreases the synthesis rate.[12]

1.8 Factors affecting biological synthesis of metal nanoparticle

The morphological characteristics of nanoparticles can be manipulated by means of various parameters temperature.Such parameters are crucial to understand the effect of environmental factors for the synthesis of nanoparticles as they play an important role during the optimization of metallic nanoparticle synthesis by biological means.

1.8.1 pH

The reaction medium pH plays an critical role in the formation of nanoparticles.Size and shape of nanoparticles vary with the pH of the medium,and large sized nanoparticles are produced in acidic pH.

1.8.2 Reactant Concentration

The formation of metallic nanoparticles is affected by the concentration of biomolecules present in the extract.Nanoparticle size can be modulated by using different extract concentrations.

1.8.3 Reaction Time

The reaction time plays an important role for synthesizing nanoparticles.In the preparation of Cerium Nitrate Hexahydrate the mixture was stirred for 10 minutes to get a homogenous solution.

1.8.4 Reaction temperature

The tempearture is a critical component which plays a key role in determining the shape,size,and yield of synthesized nanoparticles using plant. The average size of the naoparticles decreased to 10 nm with the rise in the reaction temperature to 60 degree celcius.[13]

1.9 Literature Review

Dhivya *et. al.* reported the Accumulation of phyto-mediated nano-CeO_2 and selenium doped CeO2 on Macrotyloma uniflorum (horse gram) seed by nano-priming to enhance seedling vigour.The phyto -mediated samples CeO_2 and Se-CeO_2 were studied through the analytical techniques UV-DRS,FT-IR,XRD,DLS and HIRTEM with EDAX. The XRD showed the highest intensity at an angle 25°. The XRD pattern with the molecular fraction showed that the structure of CeO_2 is FCC and the lattice parameters are a=b=c=5014 Å and α=β=γa=90°.[14]

H.Rosi *et. al.* reported the Phyto-Mediated green synthesis of CeO_2-ZnO nanoparticles using glycosmis mauritiana leaf extract.The compound synthesized was characterized by X-Ray diffraction,UV,DRS, and TEM.The results showed that the prepared materials were superior in performance as compared to undoped ZnO and CeO2 particles due, to alternation in band gap,surface adsorption and enhanced photoresponsive.The XRD pattern showed that the CeO2 has the cubic phase pattern and ZnO presented the reflections on the tetragonal phase.The absorption spectra of the CeO 2/ZnO nanocomposites showed a narrow asorption peak of 381nm and an extended absorption peak of 307nm respectively.TEM show the formation for spherical particles,it can be clearly seen that CeO2 nanoparticles have been doped with ZnO nanoparticles.The average size of the particle predict to be 14nm.[15]

Aditi Rana *et. al.* reported the Green synthesis of CeO_2 nanowires immobilized with alginate-ascorbic acid biopolymer for advance oxidative degradation of crystal violet. The material was characterized by FTIR, XRD, SEM-EDX, DSC, DLS and UV-Vis spectroscopy. The X-ray diffraction data obtained suggested a cubic fluorite structure.The value of band gap energy of the material using UV-VIS spectroscopy is 2.56 eV. SEM image represents nanowires immobilized with the layer of polymer blends with average diameter of 5nm which is found to be in close proximity with XRD results.[16]

Pandiyan Nithya *et. al.* reported the biogenic synthesis of Ag-Au bimetal doped CeO_2 nanoparticles from Justicia adhatoda. The FT-IR and Raman spectrum exhibit the peaks at 460 and 464 cm^{-1}.The insertion of Ag-Au/CeO_2 surface creates lattice defects the leads to reduce the band gap energy of Ag-Au/CeO_2 at 3.15 eV. The XRD results suggested the average crystalline size of the silver-gold loaded CeO_2 was 28nm.Raman spectrum of unloaded and Ag/Au bimetal loaded CeO_2 nanoparticles exhibits a single band at 464nm cm^{-1}. From the SEM and HR-TEM micrographs of silver-gold loaded CeO2 nanoparticles are spherically shaped in structure, and they are uniformly agglomerated[17].

Satish Arvind Ahire *et. al.* reported the Green synthesis of Ceria Nanoparticle using Azadirachta Indica Plant. The fabricated CeO_2 sensor was characterized by XRD,SEM,EDS and TEM technique.XRD confirms the formation of cubic lattice of CeO2 material.The mean nanoparticle size of cerium nanoparticles calculated was 30.57 nm[18].

Salim Ali *et. al.* reported Synergetic effects of green synthesized CeO2 nanorod-like catalyst for dedration of organic pollutants to reduce water pollution.XRD and EDAX analysis data suggested that the catalyst consisted of cerium particles covered by CeO2 having bandgap 2.34 eV.SEM and DLS confirm that the catalyst is a rod-like shape with a 23 nm average hydrodynamic size.XRD suggested a cubic a cubic structure with lattice[19].

M.Farahmandjous *et. al.* synthesized cerium oxide using cerium nitrate and pottassium carbonate precursors.Their physicochemical properties were characterized by high resolution transmission electron microscopy (HRTEM),scanning electron microscope (SEM), X-ray diffraction(XRD),cenergy dispersive spectroscopy(FTIR) and UV-Vis spectrophotometer.Xrd pattern showed the cubic structure of the cerium oxide nanoparicles.The average crystalline size of CeO2 was around 20nm as estimated by XRD pattern showed the cubic structure of the cerium oxide nanoparticles.The average particle size of CeO_2 was around 20nm as estimated by XRD technique and direct HRTEM observations.The surface morphological studies from SEM and TEM depicted spherical particles with formation of clusters.The sharp peaks in FTIR spectrum determined the existence of Ce-O stretching mode and the absorbance peak of UV-Vis spectrum showed the bandgap energy of 3.26 eV[20].

Santhoshini Priya T *et. al.* reported the synthesis of cerium oxide semiconductor in several form such as nanoparticles, beads and film using simple precipitation method, sol gel method, dip coating method respectively. The purity and crystallinty of the cerium oxide nanoparticles was found using XRD analysis.The crystalline size was found to be 10^{-18} nm using Scherrer formula. Quanta 200FEG equipment was used to study the morphological behaviour of the cerium oxide nanoparticles.The aggregation of the nanoparticles was visible from the SEM images and also well agreed with the XRD data[21].

Pragya Gopal *et. al.* reported the synthesis of cerium oxide nanoparticles from Helianthus annus seeds as an ecofriendly process. The CeO_2 nanoparticles have promising advances in medical science and therapeutic mediators in biology. For exploding the potential of nanoparticles, we have used ethanolic seed extract of CeO_2 nanoparticles was analysed by different spectroscopic mathods.UV-Vis study, the optical band gap of the synthesized nanoparticles was 4eV at 340 nm wavelength.FT-IR analysis results showed the Ce-O stretching bands by assigned peaks at 592-482 cm. X-ray diffractometer(XRD), the size of cubic structure of nanoparticles (D) was calculated by Debye-Scherrer's method.[22]

1.10 Motivation of the work

Among other nanoparticles, Cerium Oxide (CeO2) nanoparticles have been mostly exploited due to their unique surface chemistry, high stability, and biocompatibility. It is mostly used in the fabrication of sensors, cells, catalysis, therapeutics agents, drug delivery careers, and anti-parasitic ointments. Presently, CeO2 nanoparticles is mostly synthesized via two methods, such as physical and chemical. However, these methods utilize toxic reducing solvents posing several threats to the biodiversity and ecosystem. Moreover, the nanoparticles obtained with such approaches are toxic and unstable, making them less efficient. Thus, recently a safe, less toxic method has been used by researchers known as Green Synthesis. This method utilizes various biological resources such as plants, microbes, or any other biological derivative. These biological extracts have a rich source of phytochemicals such as ketones, amines, enzymes, and phenols, which are believed to be responsible for the reduction and stabilization of bulk salts into respective nanoparticles.

1.11 Aim of the work

Green synthesis of nanoparticles has many potential applications in environmental and biomedical fields. Green synthesis aims in particular at decreasing the usage of toxic chemicals. For instance, the use of biological materials such as plants is usually safe. Plants also contain reducing and capping agents. Here we present the principles of green chemistry, and we review plant-mediated synthesis of nanoparticles and their recent applications. Nanoparticles include gold, silver, copper, palladium, platinum, zinc oxide, and titanium dioxide.

In materials science, "green" synthesis has gained extensive attention as a reliable, sustainable, and eco-friendly protocol for synthesizing a wide range of materials/nanomaterials including metal/metal oxides nanomaterials, hybrid materials, and bioinspired materials. As such, green synthesis is regarded as an important tool to reduce the destructive effects associated with the traditional methods of synthesis for nanoparticles commonly utilized in laboratory and industry. The main aim is to produce nanoparticles without any toxicity to the environment.

Chapter 2

MATERIALS AND METHODS

2.1 Cerium Oxide nanoparticle

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 minerals, namely synchysite, hydroxyl baxyl 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 5.1 Å 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 CeO_2 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, CeO_2 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.

2.1.1 Semiconductor nanoparticle

Semiconductor NPs are known to possess a wealth of quantum phenomena and show unique size-dependent material properties. These materials possess properties between metals and nonmetals and therefore they have found various applications in the literature. With a change in the particle size, dramatic modifications to their electronic and optical properties take place due to the three-dimensional (3D) quantum confinement of electrons and holes when the size of the particle approaches the Bohr radius of an exciton. Semiconductor NPs are known to possess wide bandgaps and have hence shown significant changes in their properties with bandgap tuning. Therefore, they are finding applications in photocatalysis, photo-optics, and electronic devices . They have immense potential in water-splitting applications, due to their suitable bandgap and band edge positions.

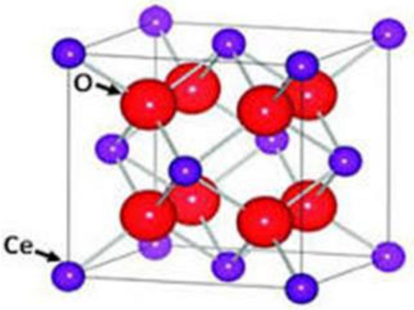

Figure 2.1 Fcc structure of cerium oxide

2.1.2 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 polishing. 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 manufacturing 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 performance. High purity Ceria are also used in phosphors as dopant to crystal.

2.1.3 Biosafety concerns of 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]

2.2 Preparation of pure cerium oxide nanoparticle

2.2.1 Materials used

Cerium nitrate hexahydrate, demineralised water, Sauropus androgynus leaves

2.2.1.1 Sauropus androgynus (L.) Merr.

(Malayalam Names: Mysore Cheera, Elakeera, Velicheera)

Sauropus androgynus, also known as sweet leaf, is a shrub grown in some tropical regions as a leaf vegetable. In Kerala, it is called madhura 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.[24][25]

Figure 2.2 Sauropus androgynus plant

2.2.4 Preparation of leaf extract

50g of fresh leaves of Sauropus androgynus (Mysore cheera) plants were taken in a beaker and 100mlof double distilled water was added. It was kept on a wire gauss and heated for half an hour. The leaf extract is filtered 2 times using normal filter paper and poured into a conical flask. About 65 ml extract was obtained.

Figure 2.3 Leaf extract

2.2.5 Preparation of Cerium Nitrate hexahydrate

About 2.171g of cerium nitrate hexahydrate was added to 100 ml of double distilled water to get 0.1 M solution. The mixture was stirred using a magnetic stirrer for 10 min to get a homogenous solution.

Figure 2.4 Solution of Cerium nitrate hexahydrate

2.2.5 Preparation of Cerium oxide nanoparticles

About 50ml of leaf extract was added to 0.1M cerium nitrate hexahydrate solution and the mixture was stirred using a magnetic stirrer for 1 and ½ hour. The colourless solution of cerium nitrate hexahydrate change into a pale yellow colour solution. The obtained solution was filtered using a Whatmann no 1 filter paper. The filtrate was allowed to dry with the help of IR lamp. After that, the powder obtained was calcinated at 500 °C for 2 hours.

Figure 2.5 Filtration after the formation of CeO_2 nanoparticles.

2.3 Preparation of Magnesium doped Cerium oxide nanoparticles

2.3.1 Materials used

Cerium nitrate hexahydrate, demineralised water, Sauropus androgynus leaves.

2.3.2 Preparation of leaf extract

50g of fresh leaves of Sauropus androgynus plants were taken in a beaker and 100 ml of distilled water was added. It was kept on a wire gauss and heated for half an hour. The leaf extract is filtered 2 times using normal filter paper and poured into a conical flask. About 65 ml extract was obtained.

2.3.3 Preparation of Cerium Nitrate hexahydrate doped with Magnesium

About 2.1711g of Cerium nitrate hexahydrate was taken. To this, 2 percent magnesium is to be added. 2 percent magnesium is about 0.043422g. For making a constant amount of Cerium nitrate hexahydrate, about 0.043422 g of cerium is removed and 0.043422 g of magnesium is added. Now the total amount of magnesium doped cerium is 2.1711g. About 2.1711g of magnesium doped cerium nitrate hexahydrate was added to 100 ml of double distilled water to get 0.1 M solution. The mixture was stirred using a magnetic stirrer for 10 min to get a homogenous solution.

2.3.4 Preparation of magnesium doped Cerium oxide nanoparticles

About 50ml of leaf extract was added to 0.1M of magnesium doped cerium nitrate hexahydrate solution and the mixture was stirred using a magnetic stirrer for 1 and ½ hour. The colourless solution of magnesium doped cerium nitrate hexahydrate is changed into a pale yellow colour solution. The obtained solution was filtered using a Whatmann no 1 filter paper. The filtrate was allowed to dry with the help of IR lamp. After that, the powder obtained was calcinated at 500 °C for 2 hours**.**

2.4 Characterization Techniques

2.4.1 X-ray Diffraction (XRD)

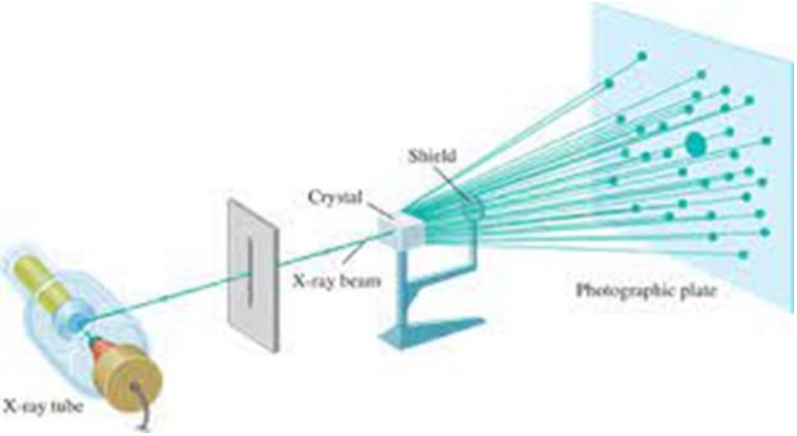

Figure 2.6 Experimental setup of X-ray diffraction

X-ray diffraction is a very important characterization technique used to study the crystal structure of materials. It provides detailed information about the structure, orientation, phases, quality and defects in the sample. The characteristic XRD pattern of each crystalline solid can be used as a fingerprint of its identification. These arrangements form a series of parallel planes with different orientations and inter-planar distances. When an X-ray beam impinges on the surface of the sample, the beam is diffracted by the crystal planes. The Bragg's equation for diffraction is[26]

$$2d\ sin\theta = n\lambda \tag{2.1}$$

where λ is the wavelength of the X-ray beam , θ the angle of diffraction ,n is the order of diffraction and d is the inter-planar spacing . X-ray diffraction broadening analysis has been used to determine the crystallite size of the nanostructures. The average crystallite size can be calculated using the Debye-Scherrer equation

$$D = \mathrm{k\lambda/(\ \beta sin\theta)} \tag{2.2}$$

Where, k is a constant (its value lies between 0.9 and 1.0 depending on the shape of the nanostructure), β is the full width at half maximum of intensity diffraction peak and θ is the Bragg's angle[27].

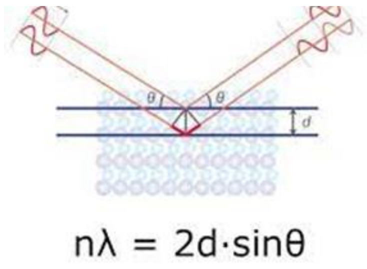

Figure 2.7 Bragg's law

2.4.1.1 Determination of crystalline size

The determination of crystalline size is very important as the mechanical and physical properties of the nanocrystalline materials strongly depend on it. In this study ,the Debye-Scherrer and Williamson-Hall equations have been used to calculate the crystalline size of the sample.

a) Debye-Scherrer Method

The average crystalline size was calculated using the Scherrer equation given by

$$D = \quad k\lambda/\beta\cos\theta \qquad (2.3)$$

where 'D' is the average crystalline size 'k', is the shape factor which depend on the crystalline shape(~0.9), 'λ' is the wavelength incident Cu-Kα radiation(1.5149Å),is the full-width at half maximum of the diffraction peaks and 'θ' is the Bragg's angle.

In Scherrer method, the influence of non-uniform strain and instrumental results on the peak broadening has not been mentioned. It suggested only a lesser limitations on the average crystalline size.[28]

b) Williamson -Hall Method

The Williamson-Hall method is a convenient procedure which includes the crystalline size and microstrain contributions to the peak broadening studies of XRD profiles .Stokes and Wilson derived the contribution of microstrain to peak broadening as[29]

$$\beta\varepsilon = 4\varepsilon \tan\theta \qquad (2.4)$$

where 'ε' is the lattice strain.

The total broadening, β is thus the sum of the broadening due to crystalline size(β_D) and that due to microstrain ($\beta\varepsilon$) given by,

$$\beta = \beta_D + \beta\varepsilon \qquad (2.5)$$

Therefore,

$$\beta = k\lambda/D\cos\theta \ + 4\varepsilon \tan\theta \qquad (2.6)$$

On arranging, the equation can be expressed as

$$\beta \cos\theta = k\lambda/D + 4\varepsilon \sin\theta \qquad (2.7)$$

The slope of the plot of ‘βcosθ’ versus ‘4sinθ’ gives the microstrain ‘ε’ and the average crystalline size can be found from the intercept which is kλ/D .

2.4.2 Ultra-Violet- Visible- Near-Infrared Spectroscopy

The energy changes associated with the transition of electrons between the outermost energy levels of a molecule lies in the radiation range from the near infrared (2500-800 nm) through the visible (800-400 nm) to the ultraviolet (400-10 nm) and the essential process of energy absorption in the ultraviolet region followed by the excitation of electrons occurs in the visible region. The wavelength at which the material absorbs the maximum amount of light is known as the absorption maximum, λmax. The hypsochromic shift (blue shift) of absorption maximum occurs when the shift in absorption is to a shorter wavelength, while the shift in absorption maximum to a longer wavelength results in the bathochromic shift (red shift). Other effects of absorptions occur when the intensity of absorption increases or decreases is called the hyperchromic or hypochromic effect, respectively.

The intensity of absorption due to the absorption of monochromatic light of wavelength λ is given by

$$\log I0/\mathrm{I} = \mathrm{kn} \qquad (2.8)$$

where $I0$ and I are the respective intensities of the incident and transmitted light, κ is the proportionality constant, and n is the number of molecules of absorbent in the light path.

For substances in solution, n is proportional to the molar concentration of the solute (c) and to the length (l) of the cell (path length) that contains the solution

$$Optical\ density\ or\ absorbance = \log_{10}\ I_0/I = \varepsilon cl \qquad (2.9)$$

This is Beer-Lambert law. The above equation gives the absorbance (A) or optical density (d) of the solution. The term ε is the molecular extinction coefficient which is the normal unit of absorption intensity. A larger extinction coefficient corresponds to the more efficient absorption.

In terms of transmittance (T) the Beer-Lambert law becomes

$$A = -T \qquad (2.10)$$

where $T = I/ I0$

The oscillator strength (f) is given by

$$\varepsilon = 0.464 \times 10^9 f/\Delta\nu \quad (2.11)$$

where Δν is the range of wavenumbers (reciprocal wavelengths) over which the electronic transition extends and f is a measure of the number of electrons per molecule taking part in the transitions responsible for the absorption of light.[27]

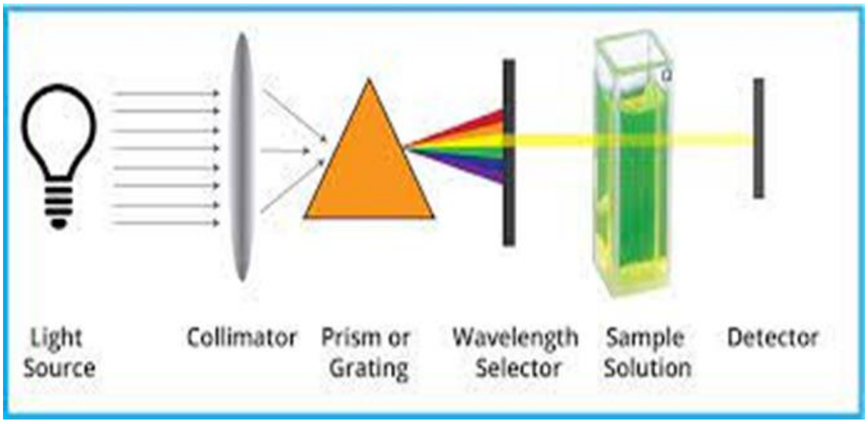

Figure 2.8 Experimental setup of UV-Vis Spectroscopy

Chapter 3

RESULTS AND DISCUSSIONS

3.1 X-ray Diffraction analysis

The structural analysis of CeO_2 nanoparticles was carried out using powder X-ray diffraction technique using Rigaku Miniflex 600 with Cu K_α (λ =1.5406A^0) radiation. The XRD spectrum of the green synthesized CeO2 nanoparticles is given in figure 3.1.

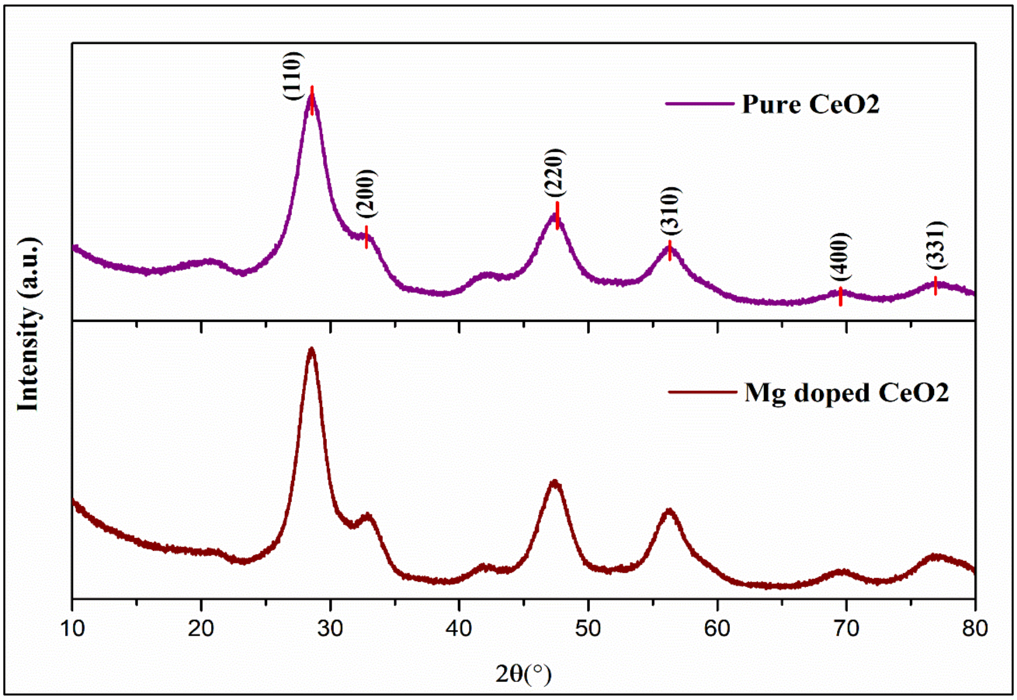

Figure 3.1 XRD pattern of CeO_2

3.1.1 Phase Identification

The pure CeO_2 sample displayed strong diffraction peaks at 2θ values 28.5°, 32.7°, 42.0°, 47.3°, 56.2°, 69.5°, 77.1° corresponding to the crystal plane (110), (200) ,(220), (310), (400), (331) and it attributes to the cubic structure of CeO_2 nanoparticles. The sharp and clear-cut peaks confirmed the high purity and crystalline nature of the prepared CeO_2 nanoparticles.

3.1.2 Crystalline size

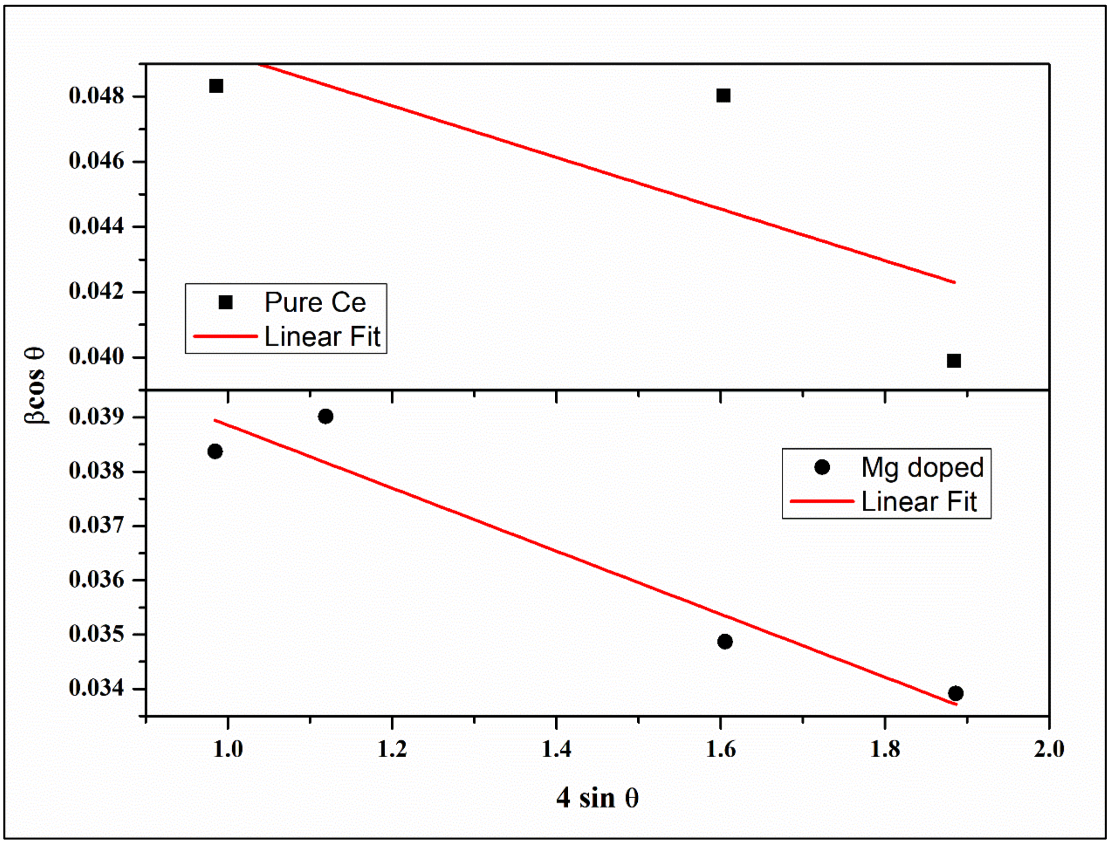

Figure 3.2 Williamson-Hall plot for biosynthesized pure and Mg-doped CeO_2 nanoparticles

The average crystalline size of pure CeO_2 and Mg doped from the W-H plot is 23.77nm and 30.45nm respectively.

The average crystalline size of the pure CeO_2 and Mg doped CeO_2 calculated using the Scherrer equation was found to be 29.28nm and 35.055 nm respectively. The crystalline size estimated from the Scherrer equation and W-H plot showed variation which may be due the difference in averaging the particle distribution.

3.2 UV-Visible Absorption Spectrum

Optical properties of biosynthesized CeO_2 nanoparticles were studied using JascoV-760 specrophotometer. Figure 3.3 shows the UV-Visible absorption spectrum of the samples recorded in the range 200-800 nm.The figure shows a strong reflectance edge at 370 nm for pure CeO_2 and at 367 nm for Mg-doped CeO_2.

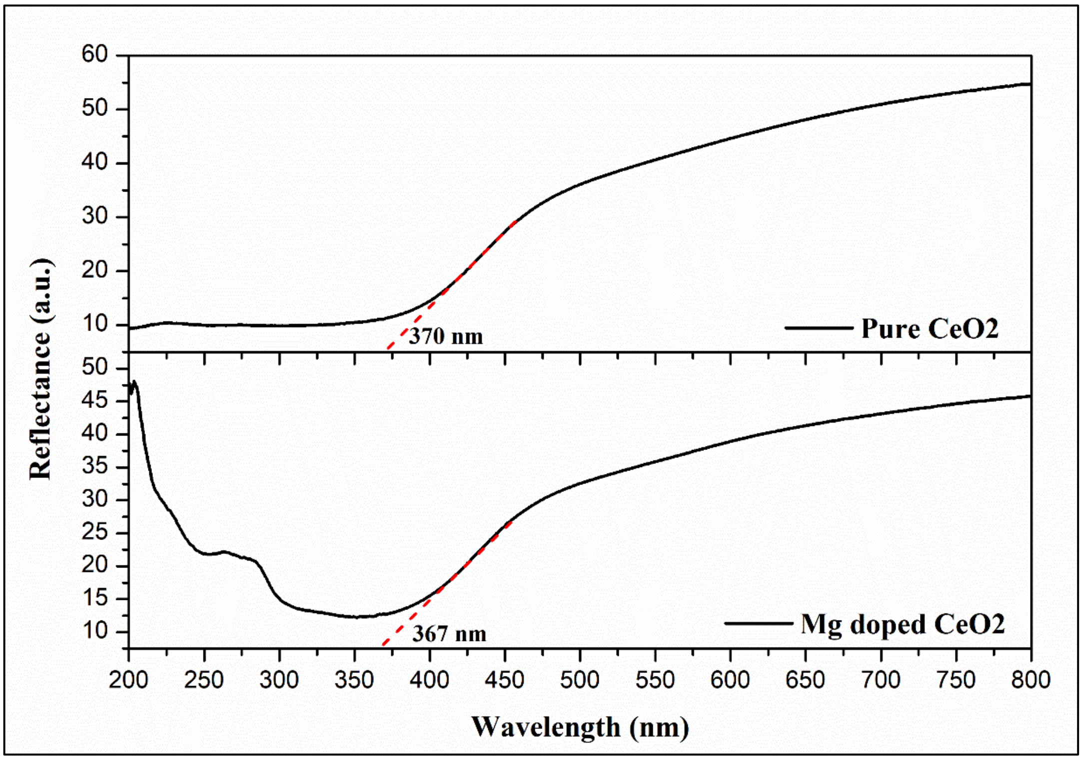

Figure 3.3 UV-Vis Absorption spectrum of biosynthesized pure and Mg-doped CeO_2 nanoparticles.

3.2.1 Determination of optical bandgap-Tauc plot

The optical band gap energy of synthesized CeO2 nanoparticles can be analysed using David and Mott expression which relates incident photon energy (hν)with absorption coefficient (α) through the Tauc plot equation

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where ‘A’ is a constant independent of energy, ‘h’ is the planck’s constant. ‘ν’ is the frequency of the incident photon,Eg is the optical bandgap energy of the nanomaterial and ‘n’ is the power factor. Depending upon the nature of the transition,n can have values 1/2, 3/2, 2 or 3 for direct allowed, direct forbidden, indirect allowed or indirect forbidden transitions repectively.In this case, the value of n is 2. The indirect bandgap energy of the synthesized CeO_2 nanoparticles can be estimated from the intercept of the extrapolated linear fit of the plotted experimental data of $(\alpha h\nu)^2$ versus the photon energy (hν) as shown in the figure. The indirect bandgap value, E_g calculated from the Tauc plot is found to be 3.28 eV for pure CeO_2 and 3.37 eV for Mg-doped CeO_2.

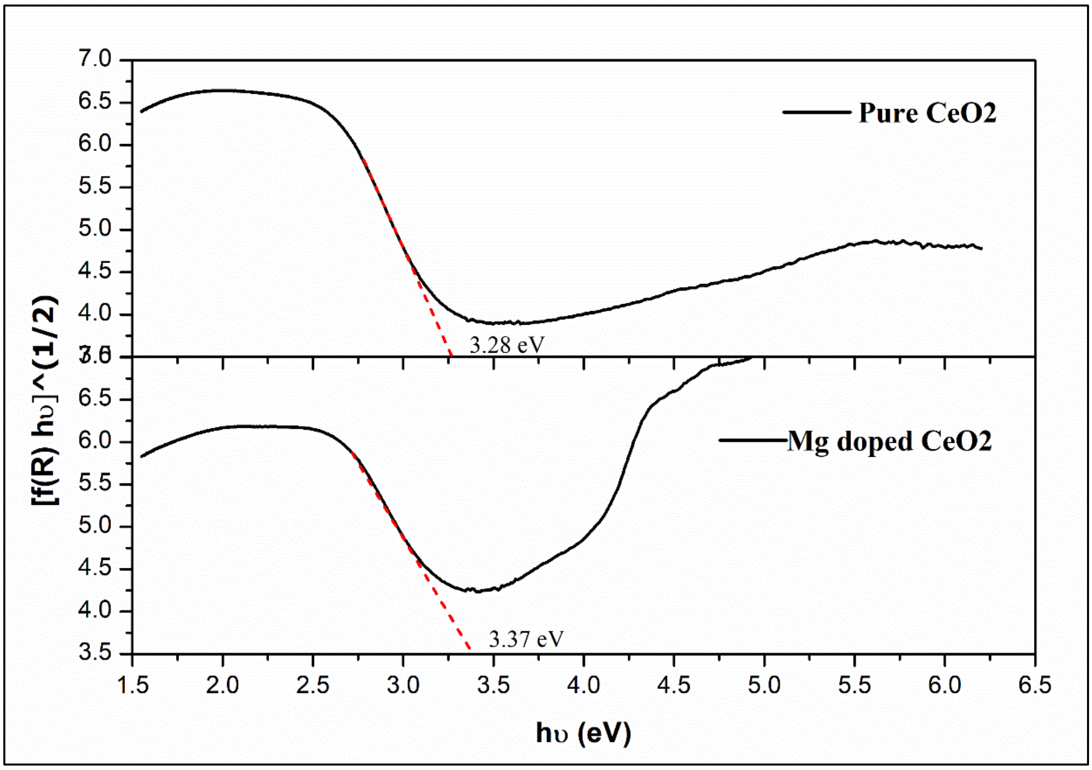

Figure 3.4 Tauc plot of biosynthesized pure and Mg-doped CeO_2 nanoparticles

Chapter -4

Summary And Conclusion

4.1 Summary

Cerium oxide nanoparticles were successfully synthesized by the cost-effective and environment friendly green synthesis method using *sauropus androgynus* extract. The structural and optical properties of the synthesized nanoparticles were characterised by XRD-UV-VIS spectroscopy. The cubic structure of the sample was confirmed by XRD analysis. It also revealed the high purity and crystalline nature of the sample with an average crysatalline size of 29.28 nm and 35.055nm for pure cerium and magnesium doped cerium respectively estimated by the Debye Scherrer formula. This showed a small variation with the one calculated from the W-H plot which was found to be 30.45nm and 23.77nm for pure cerium and magnesium doped cerium respectively. The variation may be due to the difference in averaging the particle size. The UV-Vis spectrum of the sample showed an reflectance peak around 370 nm for pure CeO2 nanoparticles while that of Mg-doped cerium appears at 367 nm. The optical bandgap of the pure CeO_2 nanoparticles calculated from the Tauc plot found to be 3.28 eV and that for Mg-doped CeO_2 nanoparticles is 3.37 eV.

4.2 Conclusion

Green synthesis is a promising method for synthesizing nanoparticles equivalent in nature of that obtained by chemical method. Instead of chemical method, this environment friendly method is recommended for the synthesis of rare-earth and other oxides. Also, the samples prepared using different plants can be checked for their biological activities as a future work.

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