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Synthesis and characterization of cerium oxide nanoparticles by antibacterial activity approach

G. Sabeena[1], S. Rajaduraipandian[2], S. Gandhimathi[2], G. Annadurai[*1]

[1]*Sri Paramakalyani Centre of Excellence in Environmental Sciences, Manonmaniam Sundaranar University, Alwarkurichi, India*

[2]*Sri Paramakalyani College, Manonmaniam Sundaranar University, Alwarkurichi, India*

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Key words: Co-precipitation method, Cerium oxide nanoparticle, Characterization studies, Antibacterial activity

Abstract

During the last decade green synthesized cerium oxide nanoparticles (CeO_2 NPs) attracted remarkable interest in various fields of science and technology. Cerium oxide nanoparticles have been used in a number of non-medical products over the years. Synthesis of cerium oxide (CeO_2) nanoparticles was studied by new and simple co-precipitation method. The crystalline structure, surface morphology, phases, functional groups and size were examined by assorted characterization techniques like scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA) and fluorescence spectroscopy studied were investigated. Furthermore, the antibacterial properties of CeO_2 nanoparticles were investigated by their bacterial activity against four bacterial strains using the agar well diffusion method.

***Corresponding Author:** G. Annadurai ✉ gannadurai@msuniv.ac.in

Introduction

In recent years, the nanoscience and nanotechnology community has moved toward a more comprehensive integration of nanoscience and nanotechnologies with other emergent technologies and topics of interests such as biotechnology, biomedical engineering, environmental remediation, dye adsorption molecular communication networks, quantum computing, and data-driven design of new materials (Rachid Seqqat *et al.,* 2019).

Cerium (Ce) is a member of the lanthanide series and is one of the most adequate of the rare earth elements. These oxidation states can auto regenerate, and cerium can switch from one state to another. This is moderately due to the indistinguishable energy of the 4f and 5d electronic states and low potential energy barrier to electron density passing round between them. In this cerium oxidation states strongly absorb ultraviolet light. Cerous Ce (3^+) absorbance is in the ultraviolet range between 230–260 nm and cerium (4^+) absorbance is in the ultra violet range between 300–400 nm. The oxygen storage capacity (OSC) of ceria, is intensely connected to how easily the cerium can change oxidation states (Vaja) *et al., 2014*) Ceria (CeO_2) is a cubic fluorite-type structured ceramic material that known crystallographic change from room temperature up to its melting point (2700±C) (Farahmandjou *et al.,* 2016).

Cerium oxide through changed valence states besides numerous crystalline constructions must have discovered for several presentations such as electronic, catalytic, adsorption, optical, electrochemical, electrical, batteries, functional materials, energy storage, magnetic data storage and sensing properties (Sher Bahadar Khan *et al.,* 2013). The CeO_2-NPs have been synthesized in several methods such as precipitation (Farahmandjoua *et al.,* 2014), sonochemical (Yan *et al.,* 2012), hydrothermal (Chunwen *et al.,* 2005), solvothermal (Yadav *et al.,* 2012), ball milling (Wang *et al.,* 2002), thermal decomposition (Feng *et al.,* 2006), spray pyrolysis (Hirano *et al.,* 2000), thermal hydrolysis (He *et al.,* 2012) and sol–gel methods (Darroudi *et al.,* 2014). Such dye-labeled particles can be used in quantitative real-space studies. Layered CeO_2 is high thermal stability, surface area and catalytic properties.

The aim of our work turned into the investigation of antibacterial residences of CeO_2 nanoparticles against a wider variety of pathogens, namely *Escherichia coli, Bacillus subtillis, Enterobacter, Staphylococcus, and Pseudomonas*. The simple co-precipitation method is easy, reproducible, controllable, and low-cost changed into used for the preparation of CeO_2 nanoparticles. Finally, the nanoparticle characterization including particle size analysis of X Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet Spectroscopy (UV), Scanning Electron Microscopy (SEM), Thermo Gravimetric evaluation (TGA) and Fluorescence Spectroscopy studied had been investigated. consequently, in the present research paintings shortly, synthesized the CeO_2 nanoparticles have been characterized by way of using spectroscopic and microscopic techniques, and their antibacterial activity effects had been discussed in Gram-positive and Gram-Negative pathogens, respectively.

Materials and methods

Experimental Section Materials

Cerium (III) Nitrate [(Ce $(NO_3)_3.6H_2O$;434.2g/mol; 99.9% purity], ammonium carbonate (NH_4HCO_3. NH_2COONH_4; 157.13g/mol; 99.9% purity), EDTA (99.9% purity) was purchased from Sigma Aldrich chemicals (Mumbai, India). These chemicals were used without further purification. Distilled water was used in all synthesis process.

Preparation of cerium oxide nanoparticles

Freshly prepared EDTA solution was added drop by drop to the solution of 0.1M cerium nitrate. This mixture solution was then added slowly into the ammonium carbonate solution (0.1M). EDTA was used to control the size of nanoparticles formed and prevent the reverse reaction. The whole mixture was then stirred for 2 (hrs). Finally, the synthesized pale yellow precipitation was filtered and washed with distilled water a number of times and heated at 60°C

for 20 hrs to eliminate excess water. The as-precipitate powder sample was calcined at 800°C for five hours in a porcelain crucible using a furnace in an ambient atmosphere.

Antibacterial activity

Antibacterial activities of the cerium oxide nanoparticles were evaluated using well diffusion method on Mueller-Hinton agar (MHA). The inhibition zones were reported in millimeter (mm). Gram-positive bacteria such as *Bacillus subtillis, Staphillococcus* and then the gram-negative bacteria such as *E. Coli, Pseudomonas, Enterobacter* for the antibacterial assay of Cerium oxide nanoparticles. Briefly, Mueller-Hinton agar (MHA) plates were inoculated with bacterial strain under aseptic conditions and wells (diameter=6mm) were filled with 50µl and 100µl of the test samples and incubated at 37°C for 24 hours (Hossein Jahangirian *et al.,* 2013).

Result and discussion

X-Ray diffraction analysis (XRD)

XRD analysis revealed the nature of the cerium oxide nanoparticles as shown in Fig.1 The synthesized Cerium oxide nanoparticles are crystalline nature.

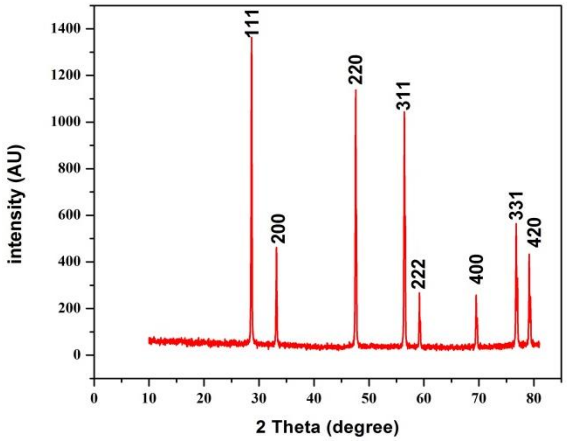

Fig. 1. XRD images of cerium oxide nanoparticles.

X-ray diffraction (XRD) was used to identify crystalline phases and to estimate the crystalline sizes. Fig. 1 shows the XRD morphology of CeO_2 nanoparticles annealed at 800°C for 3 hours. A shows the XRD patterns of Cerium oxide nanoparticles was prepared by silica aquagel confined co-precipitation method. The XRD patterns clearly show that the synthesized cerium oxide nanoparticle is identical and could be indexed to the standard CeO2 with face centered cubic structure. A plane values are (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (400), (331) and (420) of a cubic fluorite structure of CeO_2 and identified using the standard data (Farahmandjoua *et al.,* 2016*;* Kuen-Song Lin and Sujan Chowdhury, 2010*)*, cerium oxide nanoparticles and the average particle size of the cerium oxide nanoparticle is 7.3 nm. The cerium oxide powder pattern displays a random orientation that matches the typical fluorite structure for CeO_2 (Adele Qi Wang and Teresa Diane Golden, 2016). The increase of the amount of cerium salt resulted in sharper reflections, which correlates with the size of the crystalline domains. No characteristic peaks due to other impurities were observed in XRD pattern, indicating that the synthesized CeO_2 nanoparticle is pure after being calcined at 800°C in air

Scanning Electron Microscope (SEM)

The surface morphology of cerium oxide Nanoparticle is characterized by SEM indicate an accumulated thin sheet are shown in Fig. 2.

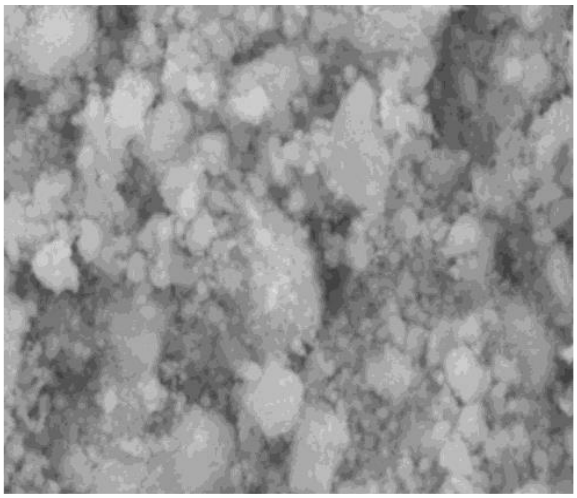

Fig. 2. SEM images of cerium oxide nanoparticles.

The Fig. 2 show the SEM images of the synthesized cerium oxide nanoparticle via precipitation method. However, the appearance of clusters in CeO_2 Nanoparticle may perhaps be due to interaction between surfaces charged CeO_2 Nanoparticle. The rough porous morphology of CeO_2 Nanoparticle changes into a

regular porous morphology revealing that CeO_2 Nanoparticle (Akhilesh Gupta *et al.,* 2010). As the particle size decreases, agglomeration will increase. Agglomeration of nanoparticles is a very common phenomenon that occurs because the nanoparticles have a tendency to decrease the exposed surface in order to lower the surface energy and the smaller particle size results in stronger agglomeration and then the morphology of the agglomerated particles is seen and the particles could not be resolved even at high magnification, it shows the well dispersed agglomerated structure of cerium oxide nanoparticle. Scanning electron microscope (SEM) images of Cerium oxide nanoparticle are shown in Fig. 2. According to Fig. 2, the surface morphology of Cerium oxide nanoparticle was observed clearly, and its homogeneous surface showed a good porosity (Jin Lin *et al.,* 2018).

Fourier-transform infrared spectroscopy (FTIR)

FT-IR studies were also conducted to investigate the structure of cerium oxide nanoparticles band at 2327 cm^{-1} is corresponded to the stretching bond of C-O (II) The intense peak at 412 cm^{-1} corresponds to the antisymmetric Ce-O-Ce stretching mode of the surface-bridging oxide (Gnanam and Rajendran, 2011; Zhan *et al.,* 2007*;* Kannan and Sundararajan, 2014*)* can be observed as shown in Fig. 3.

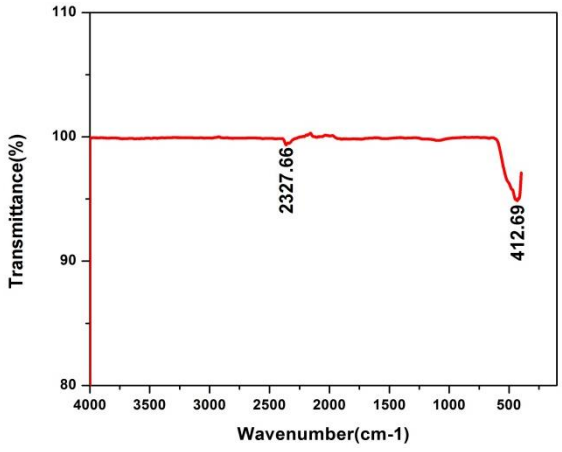

Fig. 3. FTIR image of Cerium oxide nanoparticles.

Fluorescence spectroscopy

The fluorescence spectra of the cerium oxide nanoparticles were recorded at room temperature by Fluorescence spectrophotometer and its shown in Fig. 4 fluorescence spectrum is beneficial technique for investigating energy levels. The lower emission peak at 402 nm due to the radiating defects is related to the interface traps existing at the grain boundaries. The higher emission at 645 nm may also attribute to the surface defects, and a few authors reported that these peaks are related to the dislocations or oxygen defects (Murugan *et al.*, 2016).

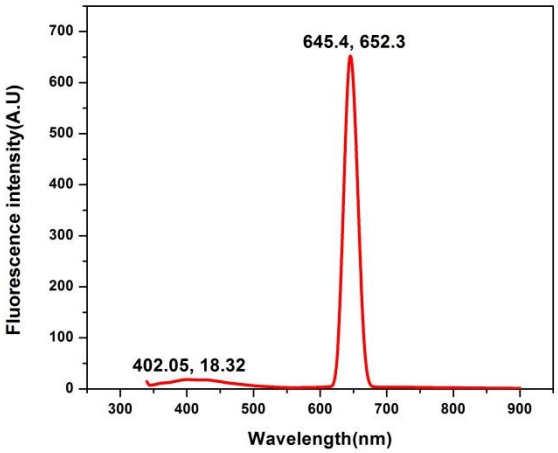

Fig. 4. Fluorescence images of Cerium oxide nanoparticles.

The fluorescence spectra of cerium oxide nanoparticle present at a series of emission in the domain 400 to 700 nm. The first band can be attributed to the electronic recombination of corresponding to the lowest emission band edge emission of cerium oxide nanoparticle at 402nm and then the higher emission band of cerium oxide nanoparticles at 645nm and then maybe attributed to the low density of oxygen vacancies during synthesis of cerium oxide nanoparticle is shown in Fig. 4 (Gnanam *et al.*, 2011).

Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) was used to study the cerium oxide nanoparticles as shown in Fig. 5 TGA plot acquired for the decomposition of cerium oxide nanoparticle is presented. The sample was heated at constant rate under N_2 atmosphere with range of 35°C/10.0(K/min)/600°C. The synthesized specimens were heated from room temperature to 100°C with an increment of 20°C/min in air. The combined curves show the cerium oxide nanoparticle (Fig. 5) From TGA data plots, it is noticed that the

weight loss of the nanoparticles is found to take place up to 700°C. The weight loss of TGA curves of the samples up to 100°C mainly corresponds to the evaporation of water, residual solvent and organic molecules (Fig. 5). The DTA curve of Fig. 5 shows a strong exothermic peak, probably corresponding to the lattice deformation of cerium oxide Nanoparticles. In addition, two exothermic peaks were observed at 348 and 394°C for cerium oxide nanoparticles (Fig. 5). It may be due to sequential events of the lattice deformation and release of the dopant ion, respectively. The corresponding weight loss is observed as shown in Fig. 5 in TGA curves. On further increasing the temperature (>400 °C), a significant weight gain is observed at 850°C these may be due to oxidation of the nitrate and acetate ions in the air atmosphere. An exothermic peak at 700°C indicates the formation of crystalline particles with phase-chemical purity (Gnanam and Rajendran, 2011; Zhan *et al.*, 2007; Kannan and Sundararajan, 2014). It was observed that the morphologies of Nanopowder can be controlled with the help of reaction methodology and type of solvents used. The soft-chemical approach is attracting more attention and it was easy to understand the chemistry involved in designing an advanced nanoparticle from a molecular precursor.

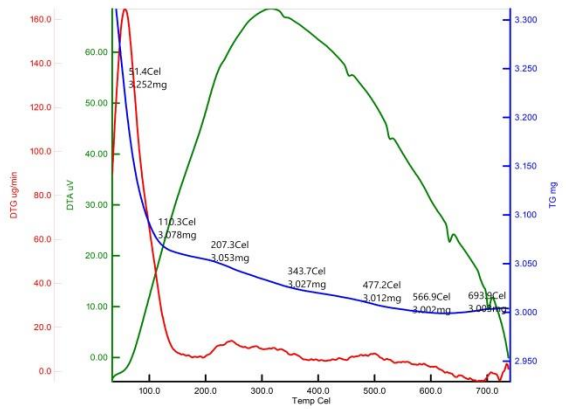

Fig. 5. TGA Curve of Cerium oxide nanoparticles.

Antibacterial activity

In the last few years, nanotechnology-based therapies have been exploited in disease diagnostics, treatment, and formulations of novel drugs. For instance, the antimicrobial potential of NPs has been mostly exploited; and has showed substantial outcomes. Presently, CeO_2 NPs have attracted great interest as an antimicrobial agent, in particular against bacterial pathogens. Evaluation of the antibacterial activity of the Cerium oxide nanoparticles solution was determined initially by the well diffusion method against different bacteria (Gnanam and Rajendran, 2011; Zhan 2007; Kannan and Sundararajan, 2014). The fig. 6 shows that the bactericidal potential of CeO_2 NPs is attributed to strong electrostatic properties, distinctive morphologies, small size, and low band energy. Due to strong electrostatic potential CeO_2 NPs interact with membrane proteins thiols groups, which results in protein denaturation, membrane impermeability eventually leads to microbial death. These bacterial strains are Gram-positive and Gram-negative species frequently encountered in infectious diseases. The results of the diameters of inhibition zones are shown in Table 1. It can be noted that the cerium oxide nanoparticles exhibited varying degrees of antibacterial activity against all bacterial strains tested (Mohamed Senouci Bereksi *et al.,* 2018) The cerium oxide nanoparticles solution was presented a strong activity against *E. Coli* with the diameter of inhibition zone of 37mm from 100µl, a weak activity against Pseudomonas with the diameter of inhibition zone of 17mm from 100µl. The mechanism of the bactericidal effect of cerium oxide nanoparticles is not very well-known. It is believed that cellular proteins become inactive after treatment with cerium oxide nanoparticles. It is also believed that cerium oxide nanoparticles after penetration into the bacteria have deactivated their enzymes, generating hydrogen peroxide and caused bacterial cell death (Zhan *et al.,* 2007*;* Kannan and Sundararajan, 2014).

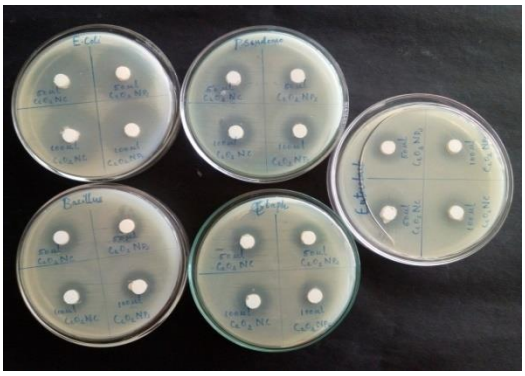

Fig. 6. Antibacterial activity of Cerium oxide nanoparticles.

Table 1. Antibacterial activity of Cerium oxide nanoparticles.

S. No	Pathogens	CeO_2 NPs Zone of inhibition inmm	
		50 µl	100 µl
1	*Bacillus subtillis*	26	30
2.	*E. coli*	35	37
3.	*Enterobacter*	30	34
4.	*Pseudomonas*	15	17
5.	*Staphylococcus*	24	25

Conclusion

CeO_2 nanoparticles have been successfully synthesized using Chemical precipitation of cerium nitrate hexahydrate and potassium carbonate. XRD spectra High purity of cerium oxide nanoparticles having crystal phase of face centered cubic (fcc) with good crystalline nature has been synthesized using a simple precipitation method with cerium nitrate compound as the precursor. SEM images indicated that with increasing temperature the morphology of the particles changes to the sphere-like shaped with less agglomeration. FTIR data exhibited the presence of Ce-O stretching mode of CeO_2. In The low cost, simplicity and efficiency of this method offer an alternative to chemical synthetic methods of cerium oxide nanoparticles. The synthesis of ceria nanoparticles and the nanoparticles showed good antibacterial property against the microorganism such as *Bacillus subtillis, E. coli, Enterobacter, Pseudomonas Staphylococcus*. Achievement of such green synthesis of ceria nanoparticles, contributes the rise of synthetic procedures using environmentally benign natural resources.

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