Biofabrication and structural characterization of cerium oxide nanoparticles

Komal Kashyap¹, F Khan¹*, Dakeshwar Verma², Sonalika Agrawal¹ Ch Chandra¹, Pradeep Kumar Dewangan¹, Vinayak Sahu¹, Padma Rani Verma¹ and Vikas Kumar Jain³

¹ Department of Chemistry, National Institute of Technology Raipur-492010, (C.G.) India
² Department of Chemistry, Government Digvijay Autonomous College, Rajnandgaon, Chhattisgarh 491441
³ Government Engineering College, Raipur (C.G.) India

*Corresponding author’s e-mail address: fkhan.chy@nitrr.ac.in, kkashyap.phd2018.chy@nitrr.ac.in

Abstract. Cerium oxide synthesis (CeO₂) nanoparticles were studied using a new and simple, eco-friendly process. The cerium oxide nanoparticles are synthesized with precursors of ammonium cerium nitrate and sodium hydroxide. Their chemical and physical properties are characterized by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Fourier transforming infrared spectroscopy (FTIR), and UV-Vis spectrophotometer scanning electron microscopy (SEM), high-resolution electron transmission microscopy (HRTEM). XRD analysis indicated the cubic structure of the nanoparticles containing cerium oxide. The standard particle size of CeO₂ was determined at 30 nm using HR-TEM and XRD. SEM determine the surface morphology of biosynthesized cerium oxide nanoparticles. A Ce-O stretching mode was defined by the strong peaks in the FTIR range, and the peak of UV-Vis range absorbance revealed the 3.26 eV band energy difference.

1. Introduction

Nanoscience and nanotechnology in science and engineering are really a recent revolutionary development that is growing at a very rapid rate [1]. Nanoparticles (NPs) are defined as products with a minimum diameter between 1 and 100 nm and are of considerable interest to numerous sciences and industries because of their specific physicochemical properties [2]. Due to their larger surface area compared to bulk equivalents, nanosized particles have various physicochemical characteristics such as stronger optoelectronics, catalytic, magnetic, and thermal conductivity [3]. Cerium oxide nanoparticles (CNPs), due to their self-regenerating antioxidant effects, have gained considerable interest in nanotechnology [4]. Cerium is a rare earth metal lanthanide and is found in two oxide phases with crystalline fluorite lattice structure in combination with oxygen [5]. Cerium oxide has been reviewed for numerous applications including electrical, catalytic, mechanical, optical, adsorption, electrochemical, battery, energy storage, practical materials, sensing properties, and magnetic data storage [6]. Ceria has achieved substantial popularity as a redox and combustion catalyst because of all of its ability to change from a reduced as well as oxidized state due to large concentrations of oxygen in...
the gas phase [7]. Several studies have been developed to aim to form CeO$_2$NPs using chemical reduction, electrochemical reduction, and photochemical reduction, such methods use extreme reducing and stabilizing agents in the synthesis process which in biomedical applications can cause some dicey effects [8]. Most of these methods, however, are complicated and/or involve either vacuum or harmful chemical compounds. In recent years, environmentally friendly and green nanoparticle synthesis has become famous for overcoming these problems. Numerous green synthetic procedures for silver and gold nanoparticles have been published [9]. The method of biological synthesis involves the use of plants (or microbes, fungi, bacteria, algae) for the protection of the synthesis of microbial crops, Plant extract is far more relevant than microbial application. The method of biological synthesis involves the use of plants (or microbes, fungi, bacteria, algae) for the protection of the synthesis of microbial crops, Plant extract is far more relevant than microbial application. Green approach with various extracts of plants, such as Prosopis farcta, Hibiscus sabdariffa, Olea europaea, Acalypha indica, and Gloriosa superba had been reported for different medical needs, for example, neurodegenerative diseases antiapoptotic, anti-inflammatory, cancer therapy, radiation safety, possible applications have been reported for biosynthesized nanoceria with different plant extracts [10]. The extracts can be derived from numerous plant parts, such as seeds, stem bark, nuts, flowers, and roots, which are also easy to collect and store and do not damage plants instead of the last and these plant extract has so many natural components, such as flavonoids, tannins, and terpenoids that are synthesized as capers and stabilizers. The use of plant extracts to develop NPs is dependent on the added benefit of the resource itself [11-13]. In the present research work, we have confirmed cerium oxide nanoparticles synthesis using Trapa natans plant extract using the green synthesis process. The synthesized nanoceria was characterized by UV-Vis spectroscopy, FTIR, XRD, EDX, and HR-TEM.

2. Experimental

2.1 Reagents and Chemicals

The chemicals used in this study have been of good quality scientific value and have been used without further purification. Ammonium cerium nitrate (NH$_4$)$_2$Ce(NO$_3$)$_6$, 99.9 % Merck), and Sodium Hydroxide solution (NaOH) were used in this study. During the synthesis, all of the aqueous solutions were prepared using Milli-Q water.

2.2 Preparation of plant extract

Before the synthesis process, the naturally accessible Trapa natans collected from the market were washed and thoroughly cleaned with deionized, double-distilled (DD) water. The fresh, clean, and dried pericarp of trapa was added to a round bottom flask consisting of an aliquot quantity of DD water and methanol at 100°C temperature to synthesize the cerium oxide nanoparticles. The wine-colored methanol solution was received after four hours of ideal condition. Then, the prepared solution was filtered. The resulting extract was stored at 4°C for the green synthesis of cerium oxide nanoparticles.

2.3 Synthesis of nanoparticles

For the biosynthesis of cerium oxide nanoparticle, an extract aliquot (100 ml) containing 40 ml of 1 mM CeO$_2$ was processed and the solution mixture has been stirred under low temperature for 24 hours. A visual evaluation has observed a change in color in the reaction mixture. Calcinated, coated, and deposited the as-prepared nanoparticles in air-tight containers before application.

3. Characterization of Cerium oxide nanoparticles

CeNP was primarily characterized by such a UV spectrophotometer (SL-159, Elico,149 India) with wavelengths ranging between 200 and 600 nm. FTIR spectra of prepared cerium oxide nanoparticles had been obtained from FTIR Spectroscopy (Bruker Optics, GmBH, Germany). Surface morphology had been identified using HR-TEM (Jeol, Japan) and XRD patterns have been calculated using a diffractometer (Xpert-Pro, England) at room temperature with a current of 30mA, 40kV, and peaks of 20.
3.1 UV-Visible Spectroscopy
The UV-Visible range has a broad absorption band at 373 nm (figure 1), possibly because the electrons are moved from the valence band (VB) to the conductive band (CB). For cerium oxide nanoparticles, the mean value was 3.324 eV reported. Besides, the bulk CeO$_2$ has an absorption peak at 357 nm (corresponding to 3.45148 eV energy) suggesting a clear blue change in the UV-Visible spectrum [13].

![Figure 1. UV-Visible spectrum of cerium oxide nanoparticles](image)

3.2 FTIR Analysis
FTIR was a valuable method for understanding the importance of functional groups in the relation between metal particles and biomolecules, for analyzing the chemical structure of the surface of cerium nanoparticles, and for detecting and effectively stabilizing biomolecules to cap nanoparticles of metal [7]. There have been many specific groups that may have been significant in micro-reducing the Ce$^{4+}$ ions (figure 2).

![Figure 2. The FTIR transmittance spectrum of cerium oxide nanoparticles.](image)
3.3 XRD
Figure 3 demonstrate the XRD pattern of the sample. All the diffraction peaks are identified and can be recorded as the cubic face-centered phase. The strong and sharp diffraction peaks indicate that the samples are finely crystallized. The high purity of the prepared ceria nanoparticles was shown by no additional peaks in the XRD. All diffractions concerning the CNPs are consistent with normal Cerianite crystallographic details (JCPDS No: 8 34-0394). This result verified the crystallization into a face-centered fluorite cubic structure of high purity single-phase CeO$_2$ [12-13]. In comparison, the diffraction peaks found at 2$\theta$ = 28.66, 33.03, 47.56, 56.39, 59.05, 69.34, 76.61 and 79.27 refer to planes (111), (200), (220), (311), (222), (400), (331), and (420) [14]. The relationship between the X-ray beam incident and the sample induces extreme X-ray reflections by constructive interference when Bragg's law is satisfied [1].

By using the Debye-Scherrer equation the average Crystallite size (D) of the synthesized CeO$_2$ nanoparticles at 500 $^\circ$ C was determined.

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where $\lambda$ stands as the wavelength of the utilized X-ray (1.5406 Å), $\beta$ is the angular peak width at half maximum in radians and $\theta$ is Bragg's diffraction angle. The PXRD peaks further demonstrate that the crystallite sizes of the obtained NPs are smaller than 30 nm, as confirmed by the synthesized CeO$_2$ images from the SEM [15].

![XRD of Cerium oxide nanoparticles using trapa pericarp extract.](image)

3.4 SEM and EDX
Scanning Electron Microscopy is performed to show particle surface morphology. Usually, the electron beam is scanned in a raster scan pattern, and the beam direction is coupled with the observed signal to build an image. SEM images can achieve a resolution above 50 nanometres. SEM has examined the surface dynamics of nanoparticles packed with cerium oxide. The above figure 4 shows the SEM picture of nanoparticles with freshly synthesized cerium oxide. The
cerium oxide nanoparticles can be observed in a spherical shape with sizes varying from 10-26 nm. From the figure 4, it can be seen that the nanoparticles of cerium oxide aggregate to form a spherical-like structure.

The energy-dispersive x-ray spectroscopy (EDX) is an observational method designed for elemental detection or chemical sample analysis characterization [1]. A standard EDX distribution as seen in the figure 4 (d) shows that Ce and O are present in the product.

![Figure 4](image_url)

**Figure 4.** (a) SEM image showing the surface morphology of the cerium oxide nanoparticles (b) SEM image showing particle size of the cerium oxide nanoparticles (c) and (d) EDX pattern of cerium oxide nanoparticles.

### 3.5 Raman Spectroscopy

Raman spectroscopy is a common spectroscopic vibration technique used to measure a substance’s molecular motion and to classify and examine molecular species by providing proof of symmetry and molecular structure (figure 5) [16].
3.6 **HR-TEM**

High-Resolution Transmission Electron Microscopy (HRTEM) data, and unique field electron diffraction patterns (SAED) have been used to examine the crystalline morphology of the CeO$_2$ sample [17]. The CeO$_2$ NPs HR-TEM picture reveals the standard particles of spherical scale are agglomerated together (figure 6). In addition, all the particles are well crystallised and a normal particle size with less than 100 nm [14].

![HR-TEM images of cerium oxide nanoparticles](image)

**Figure 6.** TEM images of cerium oxide nanoparticles.

4. **Conclusions**

Analyzing previous literature on ceria NPs showed that different methods of synthesis could provide different catalytic and physicochemical properties for cerium oxide NPs which could contribute to antioxidant or prooxidant properties [9]. The near-sphere-shaped bio-capped cerium oxide nanoparticles were successfully synthesized here via the green synthesis method using trapa pericarp extract as a reduction / stabilizing agent. The FTIR analysis confirmed that chemicals belong to the phytochemicals responsible for biodegrading behaviors. The average reduction in CeO$_2$ NPs was 80 percent of Ce$^{3+}$ ions...
within 2 days. The structural and microstructural data of these CeO$_2$NPs was collected using the techniques XRD, EDX, FTIR, and SEM.

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