Synthesis and Characterization of Nano Cerium Oxide Using Hydrothermal Technique

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Abstract: *Cerium oxide rice grain like nanoparticles have been synthesized using wet chemical hydrothermal synthesis method. Hydrothermal synthesis method provides nanoparticles with unique dimension and shape due to supercritical synthesis conditions than conventional precipitation techniques. The hydrothermal synthesis of Cerium salt in the presence of urea produces Cerium carbonate hydroxide nanoparticles with rice-grain morphology, which are reduced into Cerium oxide by heat-treating at 600°C, for 4 hours, without changing its morphology. The formation of Cerium carbonate hydroxide with orthorhombic crystal structure and Cerium oxide with cubic crystal structure were confirmed by X-Ray Diffraction [XRD] spectroscopy studies. Thermo-gravimetric analysis [TGA] in inert nitrogen atmosphere and ambient air provides the reduction temperature of hydroxide and carbonate is about 600°C. Scanning electron microscope [SEM] studies show the uniform rice grain like morphology of as-prepared Cerium carbonate hydroxide and Cerium oxide, due to the reduction at elevated temperature and crystalline structural deformation Cerium oxide shows cracks and porous on its surfaces.*

Key Words: *Cerium oxide, hydrothermal, ceramic, polishing, rare earth oxide*

1. INTRODUCTION

The use of rare earth materials on space, aviation, energy, catalyst, electronics are quietly unavoidable due to their robust physical, chemical and mechanical properties, with more excellent stability in wide ranges of operational temperature conditionals [1, 2]. The role of rare earth ceramics widely used as thermal barrier coating material for high-temperature applications, such as space, aviation and power plants [3–5]. Seventeen rare earth elements are present in the periodical table, among all elements being Cerium, Neodymium and Lanthanum found higher. Due to the strong magnetic property of Neodymium, it is intensively used for fabrication of permanent magnets for electronic devices [6–8]. Lanthanum shows excellent catalytic performance since it used in battery electrodes, hydrogen storage and catalyst for oil refineries [9–11].

Ceria based ceramic materials have the vast number of applications, such as catalyst, corrosion inhibiter, polishing, solid oxide fuel cells and so on [12–15]. Cerium oxide catalytic activity is used in solid oxide fuel cells because it allows for rapid diffusion of oxygen atoms and high oxygen ion conductivity [16, 17]. Cerium oxide also is used as an alternative of platinum in catalytic converter, as an oxygen yielding due to non-stoichiometric ability to give up oxygen without decomposing [17]. Cerium oxide reduces the air pollution by assisting complete combustion of volatile carbon species when it is added with them as an additive [18–20]. Cerium oxide powder is used in grinding and polishing of other materials due to its insolubility in polar and non-polar solvents [21].

Lanthanum-Cerium oxide is used for thermal barrier coatings because its thermal expansion coefficient is similar to the bonded coating, which leads to good adherence of the coating material on the substrate, from room temperature to 1400°C [22]. Lanthanum Cerium zirconates exhibit good characteristics in hot corrosion environment, molten salt corrosion-resistant at 900°C, without any significant degradation on coating [23].

The synthesis of the Cerium oxide through wet chemical process has many methods available, such as precipitate and co-precipitate techniques, sol-gel method, hydrothermal method etc. [15, 24, 25]. Hydrothermal synthesis of ceria oxide nano/ micro particles plays a major role due to its resulting uniform morphology and dimensional homogeneity [26–28]. Many researchers synthesized and analyzed various morphologies of cerium oxide. Hirano et al. synthesised nanocrystalline Cerium oxide using Cerium sulfate and Cerium ammonium sulphides as a precursor and urea as a buffer solution [29].

Zhou et al. synthesized Cerium oxide spears using poly vinylpyrrolidone (PVP) as a surfactant [30]. Pan et al. synthesized Cerium oxide nanorods and nanotubes using hexadecyltrimethylammonium bromide (CTAB) surfactant [31]. Guo et al. synthesized nano flower-like Cerium carbonate hydroxide and by heating at 500°C with flowing air, results in Cerium oxide particles [32]. Chung et al. synthesized Cerium carbonate hydroxide and heated at 500°C and 800°C, followed by air quenching to obtain Cerium oxide nanoparticles [33]. Li et al. identified that the reaction solution condition plays a huge role in particle size confinement in hydrothermal synthesis [34]. Thermal barrier coating nanofillers play a major role in the recent decade, due to the unique properties of nanomaterial influencing the topcoat materials [35–38].

The morphology and size uniformity of hydrothermally synthesized materials paved the way to synthesis the Cerium nanoparticles via hydrothermal synthesis for thermal barrier coating material will lead to a greater influence on the development of thermal barrier coatings. In this paper, synthesis of the Cerium oxide nanoparticles from Cerium nitrate salt as a precursor, urea was used as a size and morphology confinement material through hydrothermal synthesis method. As synthesized powder and heat-treated powder characterizations, such as XRD, SEM and TGA in air atmosphere and nitrogen atmosphere, were carried out to obtain the confirmation of formation of Cerium oxide nanoparticles and its size, morphology and thermal degradation.

2. SYNTHESIS AND CHARACTERISATION

A. Synthesis

Chemicals required: analytical grade Cerium (III) nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$] extra pure 99.9% from Sisco Research Laboratories Pvt. Ltd., urea [CH_4N_2O] extra pure 99% from Sisco Research Laboratories Pvt. Ltd., DI water and ethanol. *Synthesis Procedure:* 0.1 M of Cerium nitrate and 0.3 M of urea were dissolved in DI water, with the help of magnetic stirrer, for 5 minutes. Then, the solution was transferred into 150 ml Teflon lined autoclave reaction vessel and bolted to obtain an airtight seal. The autoclave was transferred into a hot air oven, at 180°C kept, for 8 hours, resulting white colour precipitates. The resultant precipitates washed with DI water and ethanol and then dried in a hot air oven at 120 °C, for 4 hours. The portion of resultant powder taken for characterisation and remaining heat-treated in a muffle furnace at 600 °C, for 4 hours, resulting the pale yellow colour powder.

B. Characterization

X-ray diffraction studies were done by the help of Bruker D8 Advance ECO XRCD Systems with SSD160 1D Detector instrument, used for analysing the crystallite size and phases of as dried and heat-treated samples. Scanning electron microscope studies were done by ZEISS EVO 18 SEM, used for analysing the surface morphology of the as dried and heat-treated samples. Thermo-gravimetric analysis was carried out using Q500 V20.10 Build 36 instrument, with ramp heating in N_2 atmosphere and TGA Q50 V20.13 Build 39 instrument, with ramp heating in air atmosphere, used for thermal degradation of the sample under the aerobic condition and inert atmospheric conditions.

3. RESULTS AND DISCUSSIONS

A. X-Ray Diffraction Studies

X-ray diffraction studies data matched with ICDD data card no: 00 041 0013, the peeks appear on the various planes, matched with reference peaks, which confirmed the formation of intermediate compound of Cerium carbonate hydroxide ($CeCO_3OH$ [39]). Figure 1 shows the reference data peaks and as dried powder XRD data peaks.

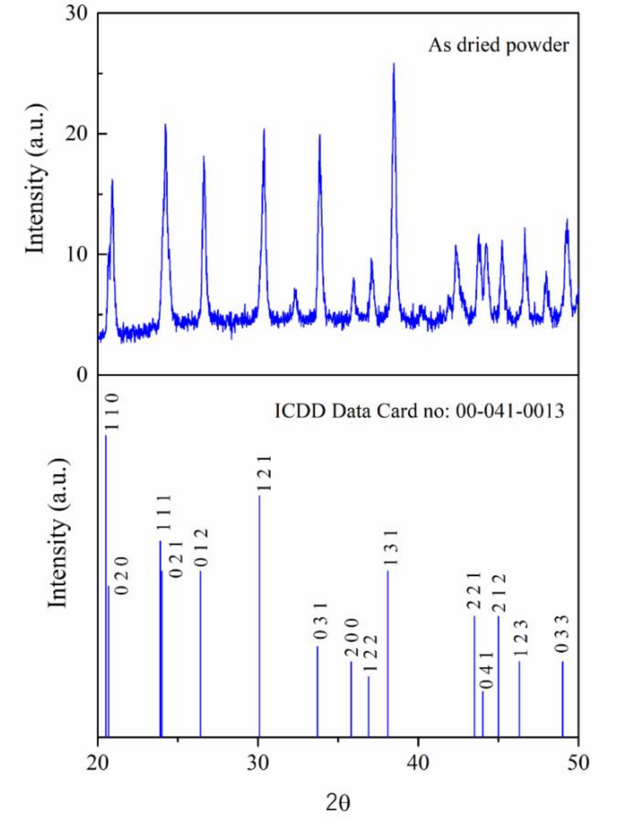

Fig. 1 – XRD peeks matching of as dried sample

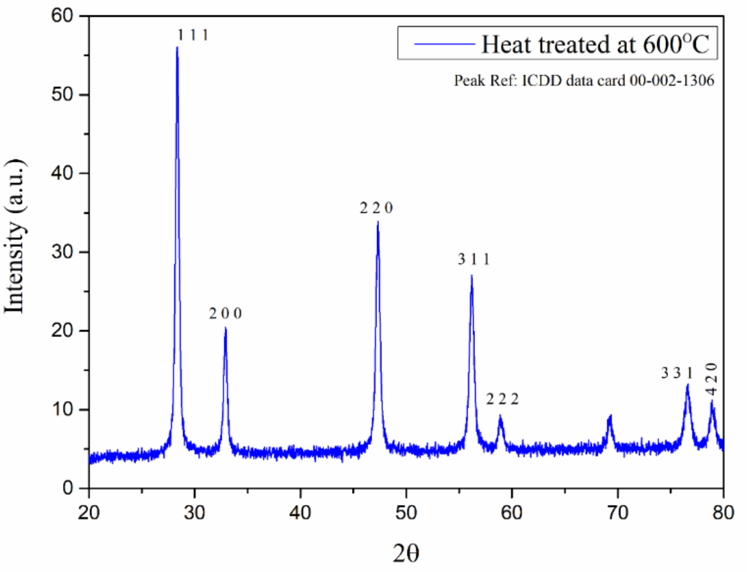

Fig. 2 – XRD peek of heat treated sample

The powders, heat-treated at 600°C for four hours, show XRD data peaks, as presented in Fig. 2. The resultant peaks matched with ICDD data card 00 002 1306, which confirms the formation of Cerium oxide.

The heat treatment results in the reduction of chemical reaction on Cerium carbonate hydroxide reduces hydrates and carbonates, resulting in the formation of Cerium oxide. Table 1 shows the crystalline size of various planes calculated by the Debye-Scherrer equation [40], founding the size of the particles ranges from 24 nm to 14 nm, for multiple reflection planes.

Table 1 – Crystalline size calculation

Sl. No	Peak position 2θ (°)	FWHM B size (°)	Crystallite size (nm)	Plane
1	28.35199	0.37243	23	1 1 1
2	32.89869	0.3678	24	2 0 0
3	47.31926	0.45684	20	2 2 0
4	56.18643	0.49091	19	3 1 1
5	58.93054	0.60675	16	2 2 2
6	76.59557	0.69387	15	3 3 1
7	78.94386	0.7961	14	4 2 0

B. Thermo-Gravimetric Analysis

Cerium carbonate hydroxide sample has undergone a thermo-gravimetric analysis in nitrogen and air atmosphere, from room temperature to 800°C. Figure 3 shows TGA analysis in N_2 atmosphere. There, the degradation of Cerium carbonate Hydroxide occurs at two stages due to anaerobic condition.

The Cerium carbonate hydroxide initially degrades the hydroxides, from 200°C to 400°C, and carbonates degrade, from 400°C to 600°C [41, 42]. The two-step degradation of Cerium carbonate hydroxide is due to the inert N_2 atmosphere, the carbonate and hydrate try to stabilize the chemical nature by forming H_2O and CO_2.

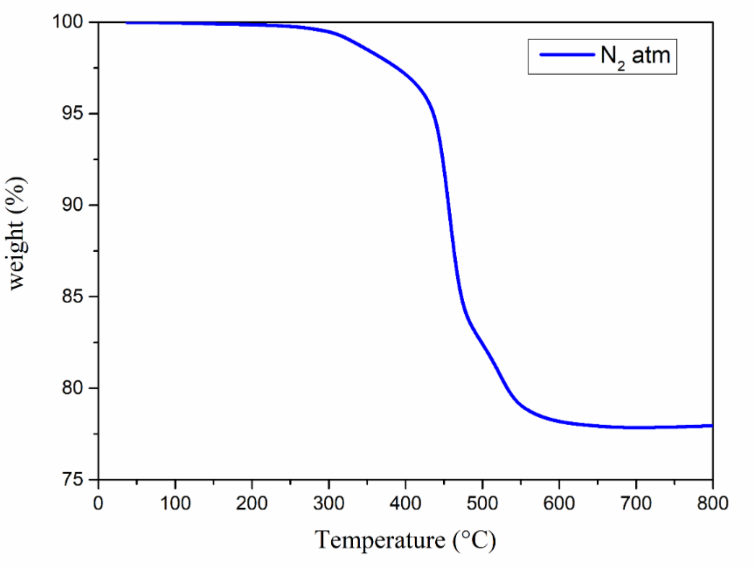

Fig. 3 – TGA studies in nitrogen atmosphere

Figure 4 shows the TGA analysis of Cerium carbonate hydroxide at ambient condition, where the degradation is occurring at a single stage due to wide abundant available of oxygen species in the environment, which require to form the more stable species, such as H_2O and CO_2 from the hydroxide and carbonate.

The initial hydroxide degrades and it is followed by the carbonate degradation. The degradation starts at 200°C and ends towards 400°C [43, 44].

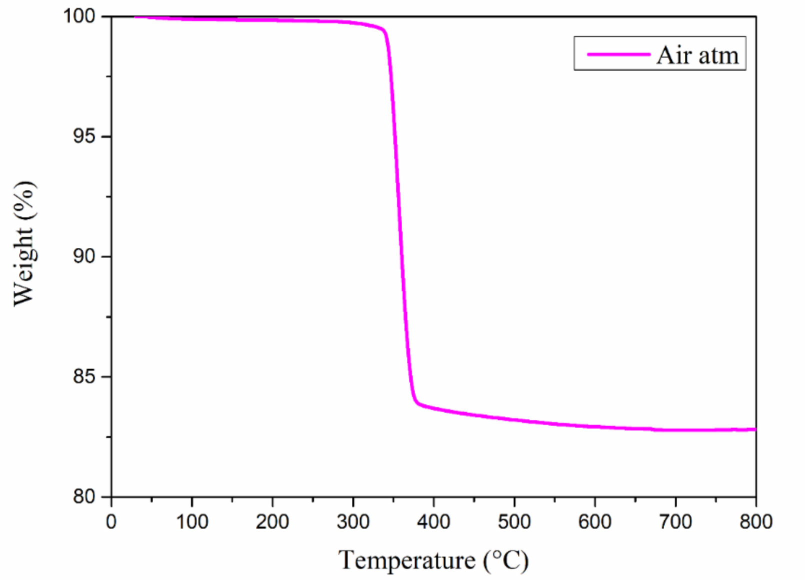

Fig. 4 – TGA studies in air

C. Scanning Electron Microscope Analysis

Figure 5 shows SEM images of as synthesized Cerium carbonate hydroxide, Fig. 5 (a), which shows the rice grain and flower-like morphology, which is owing to urea concentration [45]. The growth appears in all direction, which was shown in Fig. 5 (b), (c) and (d).

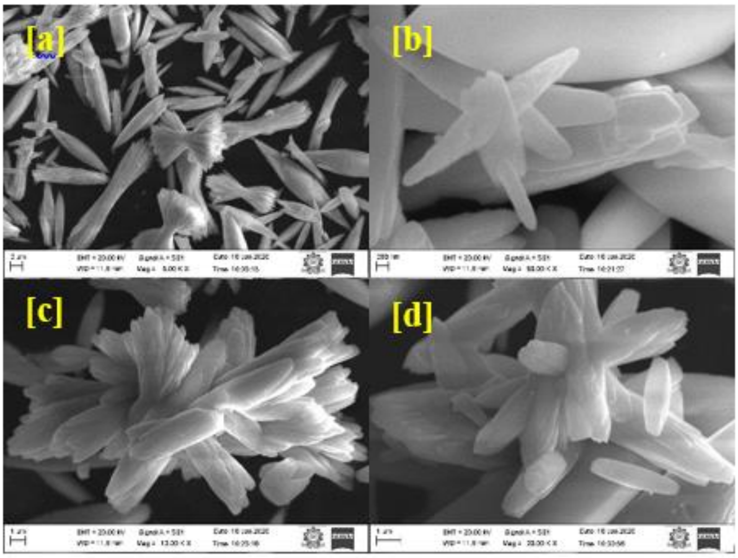

Fig. 5 – SEM images of as dried samples

Figure 6 shows SEM images of the samples after heat treated at 600°C, for four hours sample. Cracks appear on all samples (Fig. 6 (a), (b), (c) and (d)), due to the shrinkage and recrystallization, which are owing to chemical degradation of Cerium carbonate hydroxide into Cerium oxide. All the samples seem to be nanoporous due to the cleavage formed by degradation [46].

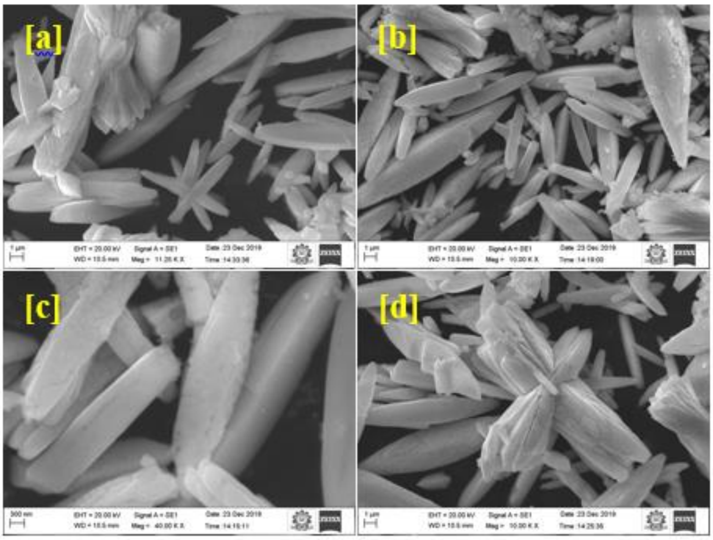

Fig. 6 – SEM images of heat-treated samples

4. CONCLUSIONS

The synthesis of Cerium oxide nanoparticles using wet chemical hydrothermal synthesis was validated through XRD studies and found the crystallite size ranges from 24 nm to 15 nm. The TGA analysis in an inert and ambient atmosphere shows the degradation potential of as dried Cerium carbonate hydroxide, which also was provided at 600°C for four hours ultimately it was reduced into Cerium oxide nanoparticles, without any structural deformation. SEM images show rice grain and flower like uniform morphology due to hydrothermal synthesis route and urea solution. The heat-treated samples show cracks due to cleavage of carbonates and hydroxides from the lattice position of crystal structure that leads to the crystal shrinkage and structural changes from orthorhombic to cubic crystal structure. The synthesized particles with nano porous structure can be used as a catalyst for applications like bio fuels, solid oxide fuel cells and hard coating material, which are for feature interest.

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