XRD, FT-IR, SEM and TGA-DTA Characterization of Hydrated Cerium Oxide Nanoparticles

Santosh M. Arade¹, Pratik M. Wankhade², A.K.Nikumbh³
¹Department of Chemistry, SMD Bharti Mahavidyalaya, Arni, Maharashtra, India
²Department of Physics, SMD Bharti Mahavidyalaya, Arni, Maharashtra, India
³Department of Chemistry, Savitribai Phule Pune University, Pune, Maharashtra, India
¹santosh.arade@gmail.com
²pwyashpm8@gmail.com

Abstract
Hydrated CeO₂ nanoparticle (CNPs) was synthesized via chemical precipitation technique at room temperature in presence of ammonium acetate. Powder XRD study reveals single phase with cubic structure. Particle size is determined by Scherrer’s equation & Scanning electron electron micrograph which exhibit in range of 50-60nm. Single stage dehydrolysis at high temperature is confirmed from thermal analysis. FT-IR analysis qualitatively confirms the formation of the title compound.

Keywords: Synthesis, XRD, SEM, Particle size, TGA-DTA.

I. Introduction
In the recent years, much attention has been drawn on the development of new synthetic paths for preparing nanostructure cerium oxide as they finds applications in various fields such as in medicine, Abrasives, Catalysts, UV blocks, Ceramics, Cosmetic Applications and opto-electronics devices and so on [1].

Several methods are available for the synthesis of nanostructure material [2-5]. Among them, chemical precipitation technique has been used in the present study, as it is easy scale up, mild synthesis condition, simple and cheap. Zhang et al. synthesized CeO₂ nanoparticles by precipitation method using alcohol-water mixed solvent [6]. Although, several report was found in the literature on the synthesis of CeO₂ nanoparticles at more than room temperature [7-9]. However, synthesis of CeO₂ nanoparticles at room temperature has an advantage of no aggregation of particles and a very small size [10]. Zhang et al. synthesized CeO₂ nanoparticle at room temperature by mixing HMT with CeO₂ nitrile solution [11]. Synthesis, formation, assembly and application of metal oxide nanoparticles were summarized in the book written by Markus Niederberger, Nicola Pinna [12].

Liu et al. synthesized cerium dioxide nanoparticles using ammonia-water solution. They were successful in obtaining particle in the range 100-200 nm [13]. So, in the same foot print, we tried to use ammonium acetate as solution. It is expected that, ammonium acetate can be used to control morphology, size & agglomeration of hydrated ceramic oxide nanoparticles.

In the present study, CNPs were successfully synthesized using chemical precipitation technique at room temperature in presence of ammonium acetate. The properties of the material were characterized by powder XRD, Scanning electron microscope (SEM), TGA-DTA.

II. Experimental

Material synthesis
The Starting materials were Cerium nitrate hexahydrate, ammonium acetate and conc. Aq. NH₄OH with an equivalent concentration of 1.1 mol L⁻¹. Ammonium solution was taken in exess during precipitation to achieve pH 9.5-10. In each of experiments, cerium nitrate hexahydrate was dissolved in double distilled water and dropwise aqueous NH₄ was added slowly added with vigorous stirring at room temperature. Precipitation began immediately with characteristic gelation of the mixture. The gel was stirred for 20 min. to achieving a homogenous mixture. The gel resulting was divided into four parts. The gel solution was added into with and with different concentration of ammonium acetate solutions. Each solution was stirred for 5 min and then left to age 7 days at room temp. After 7 days, the resulting product was washed several times by centrifugation at 3000 rev min⁻¹ with dil. NH₄OH maintaining pH 9.5-10 throughout the experiment and then once with double distilled water. The final product dried in oven at ~100°C and grind into fine powder.
Characterization

The powder X-ray diffraction pattern was determined on Regaku MiniFlex Diffractometer using CuKα radiation (λ=1.5405, nickel filter). The surface morphology study was performed using scanning electron microscope (SEM) (Model: Philips SEM, model 30 XL). TGA-DTA analysis was performed on the instrument DTG-60H simultaneous differential thermal analyzer (Shimadzu, Japan) within the temperature range 32-800°C.

III. Results and discussion

Powder XRD

The powder X-ray diffraction (XRD) pattern of the synthesized hydrated CeO₂ nanoparticles using ammonia acetate is shown in Fig.1. The diffraction peaks of the nanoparticles are quite broad indicating the crystalline size of the sample is very small. No peak of any other phase has been observed indicating high purity of the sample. The hydrated CeO₂ displays cubic structure with lattice parameter of 0.554nm. The crystalline size <D> of CeO₂ has been calculated using Debye- Scherrer formula;

\[ <D> = \frac{0.94 \lambda}{\beta \cos \Theta} \]

Where ‘λ’ is the wavelength, β is the full width half maxima, ‘Θ’ is the Bragg’s angle. The calculated crystallized size and lattice parameter of hydrate ceramic oxide nanoparticle material is tabulated in Table 1.

As can be seen from this table, the particle size is quite small in the range 50-60nm.

FT-IR Morphology study

SEM image of CeO₂ nano-powder is as shown in Fig.

Table 1. Band and corresponding peak assignment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameter (nm)</th>
<th>Mean crystallite size (nm)</th>
<th>Average particle size in nm (From SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>a=b=c=0.554</td>
<td>22.70</td>
<td>59.70</td>
</tr>
</tbody>
</table>

The FT-IR spectrum of hydrated CeO₂ is as shown in Fig.
Table 2. Bands and corresponding peak assignment of CNPs.

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>Peak Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3421</td>
<td>υ HOH</td>
</tr>
<tr>
<td>1562</td>
<td>υ bending –OH groups</td>
</tr>
<tr>
<td>567</td>
<td>υ Ce-O</td>
</tr>
<tr>
<td>465</td>
<td>υ Ce-O</td>
</tr>
</tbody>
</table>

The bands at around 3400 cm⁻¹ correspond to presence of lattice water. The band around 1570 cm⁻¹ corresponds to –OH group present in the title compound. The bond originates from the absorption of H₂O. The stretching bands near 565 and 465 cm⁻¹ assigned to bonding of Ce-O bonds [13]. The presence of bond at 3421 and below 700 cm⁻¹ qualitatively confirms the formation of hydrated cerium oxide nanoparticles. The bond and corresponding peak assignment are tabulated in Table II.

**SEM**

The SEM image of CNPs is as shown in Fig.3. It shows that particles tend to agglomerate during centrifusing & drying or during synthesis process. The formation of agglomerate was most likely due to Vander-Wall’s interaction between crystallites. Average particle size of ceramic oxides is given in Table 1.

**TGA-DTA**

TGA-DTA curve of hydrated cerium oxide nano-powder under normal atmosphere condition is as shown in Fig.4. The study has been carried out in the range 32-800 °C. The peak in DTA curve is observed at 325 °C. TGA curve indicate 4.903 percentage mass losses while the calculated one is 4.969 percentages at 325 °C. It is
evident from the graph, the single state change behaviour. Thermal study confirms the formations of hydrated cerium oxide nanoparticles at room temperature. The hydrated group has been evolved at high temperature.

![TGA-DTA spectrum of CNPs](image)

**Fig. 4.** TGA-DTA spectrum of CNPs.

### IV. Conclusions

Hydrated CeO$_2$ nanoparticles was successfully synthesized by chemical precipitation method at room temperature using ammonium acetate. FT-IR spectral analysis qualitatively confirms the formation of title compound. Thermal analysis indicates single stage dehydration to form hydrated cerium oxide. At high temperature high temperature, cerium oxide nanoparticles are formed. XRD study confirms the title compound synthesized into cubic structure with single phase. The calculated particle size of hydrated CeO$_2$ nanoparticles was in the range of 50-60nm confirms from XRD and SEM.

### V. References