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Synthesis of Cerium Oxide Nanoparticles Using Chemical Precipitation Method and Study Their Properties

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ABSTRACT
In these studies, cerium nitrate (Ce (NO3) 3.6HO), a raw material, and sodium hydroxide, a precipitating agent, were employed to create cerium oxide (CeO2) nanoparticles with a diameter of 10-39 nm . XRD, FT-IR, FE-SEM, EDS, and DLS were used to analyze CeO2 nanoparticles that had already been synthesized. The cerium oxide nanoparticles underwent calcination at a temperature of 600 °C. Using Debye Scherrer's Equation, the crystal volume was calculated and determined to be between 8 and 11 nm. Cerium oxide nanoparticle production was confirmed by the FTIR spectrum's absorption (Ce-O stretch) band at 540 cm1. The spherical shape of the CeO2-NPs structure at 39 nm could be seen in the FE-SEM pictures, and the polycrystalline nature of CeO2-NPs could be shown in the particular area diffraction pattern. The element content was given by the EDS result (Ce = 76.5, O = 16). According to studies, CeO2 NPs have an average size of around 154 nm.

Keywords: cerium oxide nanoparticles, synthesis; Chemical deposition methods.

1. Introduction
Due to its applications in numerous fields of science and technology, including high-storage capacitor devices, buffer layers for conductors, fuel cells, polishing materials, UV blocks and optical devices, such as chemical vapor deposition, electrochemistry, templates, photo-induced conversion, biological synthesis, etc., much effort has been put into developing new synthetic routes for producing nanostructure cerium oxide in recent years [1-3]. Precipitation has received the interest among them due to its benefits of being easy to scale up, simple to utilize, and inexpensive. For instance, Qiuli et al. [4] used cerium nitrate and ammonium acid carbonate as precipitation agents to create particles of CeO2 that were around 90 nm in size. Y. H. LIU et al. [5] Cerium oxide nanoparticles were created by precipitating them, and the effects of the precipitant and calcine temperature on the crystal size and shape were studied. Although the precipitation process has been widely explored to produce CeO2 particles, most earlier papers mainly addressed the impacts of cerium precursors, ligands, and additives to reaction fluids. [6, 7] Nadeem and co. [8] The synthesis mechanism from numerous sources, including plants, microorganisms, biological products, and biomedical applications, is explained together with recent developments and conceptions of CeO2 NPs. [9] It was found that the four CeO2 nanoparticle forms—sphere, octahedron, hexahedron, and bamboo-like—possess distinctive morphologies that are entirely distinct from one another and have been shown to operate as enzyme mimics with peroxidase activity. At the same time, the influence rules made it clear that CeO2 nanoparticles show outstanding catalytic activity and reusability, indicating their potential use in industry. In this paper, the precipitation chemical method was used to successfully synthesize cerium oxide nanoparticles. The materials' characteristics were assessed using a variety of techniques, including dynamic light scattering (DLS), X-ray diffraction analysis, field emission scanning electron microscopy (FE-SEM), energy-dispersive X-rays (EDX), and Fourier transformed infrared spectra (FT-IR).

2. Experimental
All chemicals from Sigma Aldrich and BDH were of the reagent grade and could be used directly.

2.1. CeO2 NPs are synthesized by chemical precipitation method: CeO2 NPs were synthesized using cerium nitrate (2.5 mol/L). Cerium salt solution was stirred continuously while 1 mol/L of sodium hydroxide solution was added dropwise to achieve a pH of about 14. After adding NaOH, a yellow precipitate of cerium hydroxide nanoparticles (Ce (OH) 3 NPs) forms that is collected and repeatedly

washed with distilled water until the pH reaches 7.The precipitate is then dried for nine hours at 75 °C, followed by nine hours of calcination at a temperature of 600 °C, producing the final product (CeO2 NPS).

3. Results and Discussion

3.1. Infrared spectroscopic analysis (FTIR): The solution is prepared and the precursor solution, which has a pH of 5.2, only includes Ce3+ soluble species, predominantly Ce3+ ions, as a result of the cerium (III) nitrate salt dissolving in accordance with the following process [10].

$Ce(NO3)3.6H2O + H2O \rightarrow Ce3+ + 3NO3- + 6H2O$

Upon pH increase, Ce3+ Ce(OH)3 NPs can precipitate into according to:

$Ce3+ + 3OH- \rightleftharpoons Ce(OH)3$ NPs

When performing a calcination process of Ce(OH)3 NPs at 600°C to obtain CeO2 NPs:

$Ce(OH)3$ NPs $\rightleftharpoons CeO2$ NPs

The FT-IR spectra of the precursor Ce(OH)3 NPs and CeO2 nanoparticles as they were generated are given in Figures 1 and 2. The time period of our research is interesting due to the apparent stability of the extremely tiny Ce(OH)3 nanoparticles. Below 648 and 667 cm-1, the ensuing range of Ce-O stretch frequency may be detected. FTIR analyses led to the discovery of cubic-shaped CeO2. One of the most unique ranges has a peak at 540 cm-1 that was associated with the phonon mode of CeO2 NPs' cubic form. The hydroxyl group of $Ce(OH)_3$'s centered OH group at 3,417 cm-1 has a -OH stretching vibrationThe absorption bands, which correspond to the frequency of vibration (OH) mode of water molecules (H-bonded) and (OH), were discovered at 1604 and 3406 cm-1, respectively.[11] By calcining, Ce(OH)3 nanostructures were thermally changed to CeO2 NPs without changing their form. Broadband with a characteristic of less than 667 cm-1 has been identified as Ce-O stretch mode.

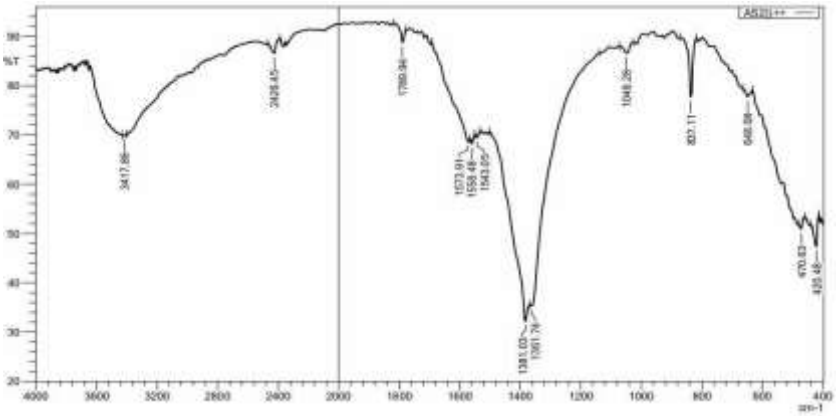

Fig. 1: FT-IR analysis of $Ce(OH)_3$ NPs

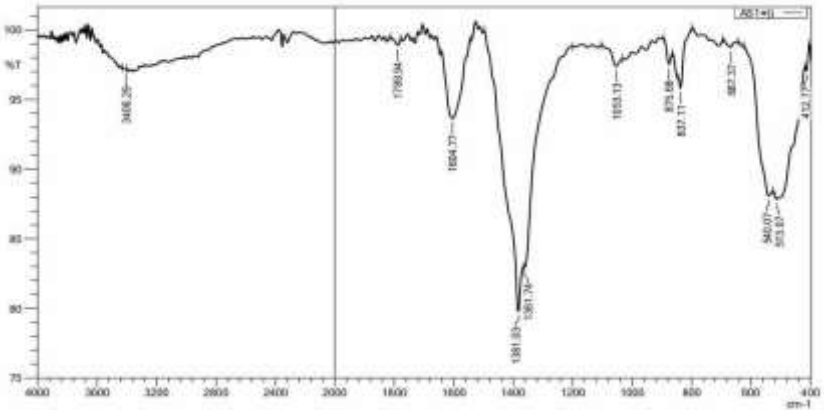

Fig.2: FT-IR analysis of CeO_2 NPs

3.2. XRD analysis: Nanoparticles were created using NaOH as a precipitate, as seen in Figure 3's powder X-ray diffraction pattern.

The (111), (200), (220), (311), (222), (400), and (331) planes' corresponding peaks are located at 2θ as shown in table 1. The powder patterns were discovered to be mostly consistent with JCPDS Standard Card No. (JCPDS-34-0394) [12]. At any of the subsequent phases, there was no peak to be seen, demonstrating the product's purity. Characterization of the diffraction peaks of CeO2 particles produced using NaOH as a precipitating agent reveals that the samples' average crystal size is extremely small—around 10.43 nm.

The Scherrer equation is used to find the average crystal size (D) for CeO2NPs :

$D = 0.9\ \lambda / \beta \cos \theta$

where D is the crystal size, k is the form factor (k = 0.9 in this work), is the Bragg angle, the incident X-ray wavelength is 1.5406, is the full width at half

maximum (FWHM), and (hkl) are Miller's indices. Using the equation shown below [13], the lattice constant (a), the dislocation density (δ), and the exact intensity (ε) can be determine d = a/√h2+k2+l2 …….. ε = β cos θ/ 4 …….. δ=1/D2

Table 1 reports the lattice constant (A°), micro strain, and dislocation density (lines/m2) data.: Data values of the X-ray diffraction of the CeO_2 NPs.

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d- pacing [Å]	Rel.Int. [%]	Tip Width	khl	D (nm)	$\delta*10^{-3}$ lines/m^2	ε $*10^{-3}$	a (A°)
28.44464	1903.553	0.7872	3.13791	100	0.9446	111	10.88	8.448	6.04	
33.10421	569.6267	0.7872	2.70611	29.92	0.9446	200	11	8.264	5.755	
47.36935	1099.103	0.8856	1.91917	57.74	1.0627	220	10.24	9.537	5.234	
56.26192	908.7019	0.7872	1.63511	47.74	0.9446	311	11.96	6.991	3.815	2.287
59.12369	171.7518	0.984	1.56262	9.02	1.1808	222	9.7	10.628	4.407	
69.49675	174.9003	0.984	1.35258	9.19	1.1808	400	10.27	9.481	3.008	
76.81468	337.5243	1.1808	1.24095	17.73	1.417	331	8.97	12.428	2.35	

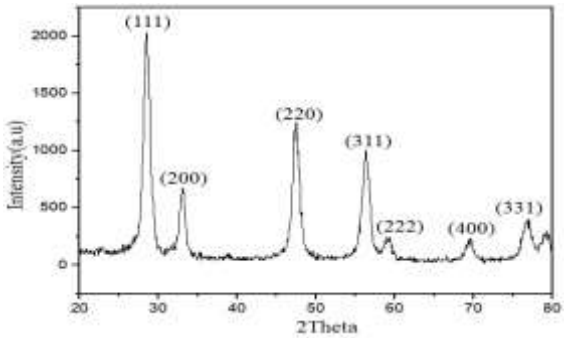

Fig. 3: XRD for Synthesis CeO_2 NPs

3.3. FE-SEM analysis: Figures 4A and B display the FE-SEM images of Ce(OH)3 and CeO2-NPs, respectively. As can be observed, it was discovered that Ce(OH)3 and CeO2 NPs occurred in globular clusters and had average sizes of 33.28 and 39.98, respectively.

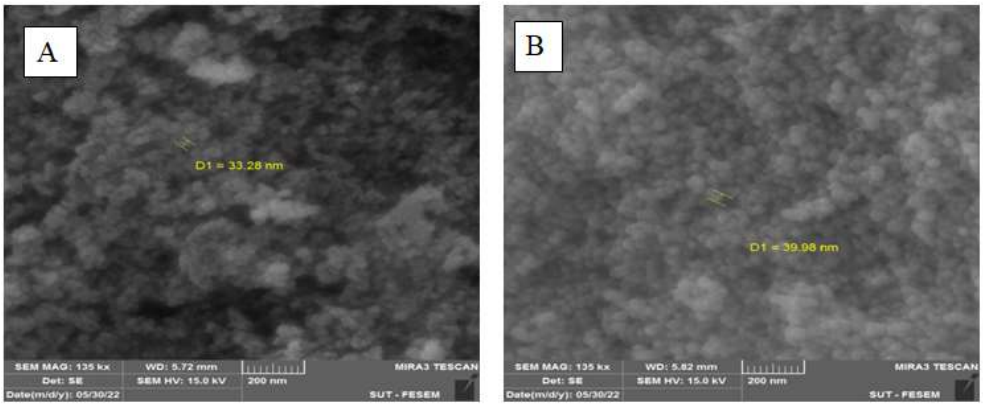

Fig.4: FESEM images of (A) $Ce(OH)_3$ NPs and (B) CeO_2 NPs

3.4. EDS Analysis: Figure 5 displays the energy-dispersive X-ray spectroscopy (EDS) results of CeO2 NPs produced using the chemical precipitation approach. The element percentages obtained from EDX were (Ce= 76.5 and O= 16), which showed the CeO2 NPs. formation with acceptable purity

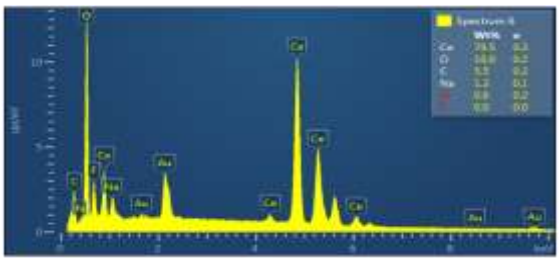

Fig. 5: EDS analysis of the CeO_2 NPs

3.5. DLS Analysis The analysis of the nanoparticle distribution of the sample is carried out through the DLS technique, taking into consideration, each particle moves in a Brownian motion independently of the other, and this is called the Doppler effect. Based on Figure 6, the average particle size CeO2 NPS 154 nm was calculated.

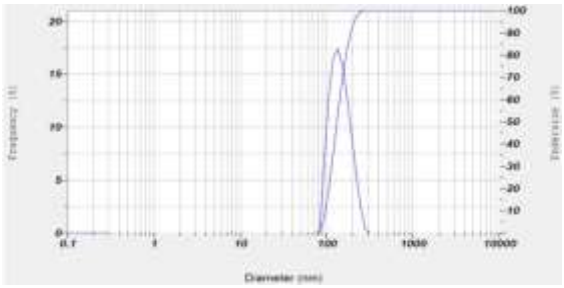

Fig. 6: Dynamic light scattering (DLS) pattern

4. Conclusions

Ce(OH)3 was generally synthesized using the chemical precipitation technique and its characteristics were investigated. The production of CeO2 NPs was effectively shown by the results of FTIR, XRD, DLS, FE-SEM, and EDS methods. The production of CeO2 NPs was effectively shown by the results of FTIR, XRD, DLS, FE-SEM, and EDS methods. Below 667 cm-1, the strong CeO2 NP band was seen. Ce(OH)3 and CeO2 NPs had spherical forms with diameters of 33 and 39 nm, respectively, according to FE-SEM investigation. Aspects of CeO2 NPs were revealed by EDX data. A narrow nanoparticle size distribution of around 90 nm to 400 nm, with an average size of 154 nm, was obtained using DLS for CeO2 NPs produced by the chemical deposition approach.

References

1. Zhiyan Guo, Fangfang Jian and Fanglin Du. A simple method to controlled synthesis of CeO_2 hollow microspheres. Scripta Materialia 61 (2009) 48–51
2. Devadoss Mangalam Durai Manoharadoss Prabaharan, Karuppasamy Sadaiyandi, Manickam Mahendran, Suresh Sagadevan. Structural, Optical, Morphological and Dielectric Properties of Cerium Oxide Nanoparticles. Materials Research. 2016; 19(2): 478-482
3. Kang Li, Pusu Zhao. Synthesis of single-crystalline $Ce(CO_3)(OH)$ with novel dendrite morphology and their thermal conversion to CeO2. Materials Research Bulletin. 45 (2), 2010, 243-246
4. Qiuli ZHANG, Zhimao YANG, Bingjun DING. Synthesis of Cerium Oxide Nanoparticles by the Precipitation Method. Materials Science Forum.610-613 (2009), 233-238.
5. Y. H. Liu et al. Synthesis and character of cerium oxide (CeO_2) nanoparticles by the precipitation method. Metabk. 53(4) 463-465 (2014).
6. M. Farahmandjou, M. Zarinkamar, T.P. Firoozabadi. Synthesis of Cerium Oxide (CeO_2) nanoparticles using simple CO-precipitation method. Rev. mex. fis. vol.62 no.5. 2016
7. Muruganantham Chelliah, John Bosco Balaguru Rayappan and Uma Maheshwari Krishnan. Synthesis and Characterization of Cerium Oxide Nanoparticles by Hydroxide Mediated Approach. Journal of Applied Sciences.12 (16).1734-1737. 2012.
8. Muhammad Nadeem, Ramsha Khan, Komal Afridi, Akhtar Nadhman, Sana Ullah, Sulaiman Faisal, Zia Ul Mabood, Christophe Hano, and Bilal Haider Abbasi. Green Synthesis of Cerium Oxide Nanoparticles (CeO2 NPs) and Their Antimicrobial Applications: A Review. Int J Nanomedicine. 2020; 15: 5951–5961.
9. Fanming Meng, Zhenghua Fan, Cheng Zhang, Youdi Hu, Tao Guan, Aixia Li. Morphology-Controlled Synthesis of CeO2 Microstructures and Their Room Temperature Ferromagnetism. Journal of Materials Science & Technology. 33(5), 2017, 444-45.
10. P. Abellan, T. H. Moser, I. T. Lucas, J. W. Grate, J. E. Evans and N. D. Browning. The formation of cerium (III) hydroxide nanoparticles by a radiation mediated increase in local pH. RSC Adv., 2017, 7, 3831-3837.
11. Motaharesadat Hosseini, Issa Amjadi, Mohammad Mohajeri and Masoud Mozafari. Sol–Gel Synthesis, Physico-Chemical and Biological Characterization of Cerium Oxide/Polyallylamine Nanoparticles. Polymers 12(7):1444. 2020
12. J. Roggenbuck, H. Schäer, T. Tsoncheva, C. Minchev, J. Hanss, M. Tiemann, Micropor. Mesopor. Mat. 101 (2007) 335-341.
13. Muruganantham Chelliah, Journal of Applied Sciences, 12,1734-1737 (2012).
14. V. Ramasamy, V. Mohana, V. Rajendran. Characterization of Ca doped CeO_2 quantum dots and their applications in photocatalytic degradation. OpenNano 3, 38 (2018).