

SYNTHESIS OF CERIA NANOPARTICLES: EFFECT OF ALCOHOL/WATER RATIO ON THE MORPHOLOGY AND CRYSTAL STRUCTURE

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ABSTRACT

In this study, ceria nanoparticles were synthesized via one of the simplest methods, which is the precipitation method. The effects of three different ethanol/DI water ratios (i.e. 1:1; 1:4; 0:1) and post-heat treatments (i.e. drying only and drying + calcination) on the crystal structure and morphology of the ceria nanoparticles have been investigated. The characterization of the ceria nanoparticles was conducted using X-Ray Diffractometer (XRD) for the crystal structure and Transmission Electron Microscopy (TEM) for the morphology. From XRD analysis results, the comparison of the highest XRD intensity peaks (at $2\theta = 28.6^\circ$) of the ceria nanoparticles samples showed that all the ceria nanoparticles samples with drying + calcination treatment were higher than the ones with drying treatment only. Additionally, the XRD peaks were analyzed using a well-known Scherrer's equation to determine the average crystallite size of the ceria nanoparticles. It was found that the ceria nanoparticles sample prepared using the ethanol/DI water ratio of 1:1 (i.e. Ceria-C1) had the biggest average crystallite size (i.e. 14 nm). Nevertheless, the TEM analysis showed that Ceria-C1 showed better morphology and dispersion compared to other Ceria samples and also clearly exhibited sphere-like nanoparticles. This finding can be associated with the dispersion stability analysis, which showed that the suspension of Ceria-C1 shows a little bit better dispersion compared to other Ceria samples.

Keywords: Cerium Oxide, Precipitation, Ethanol/Water Mixture, TEM, XRD

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INTRODUCTION

Nanotechnology is technology to produce and utilize nano-size materials.¹ In recent years, the development of the nanotechnology field has greatly advanced. The nanoparticles or nanomaterials have attracted great interest among researchers and have been studied in various fields of applications, such as the industrial, environmental, and medical fields.² It was due to their unique properties e.g. size, shape, high surface area to volume ratio, and unique mechanical, electrical, magnetic, and optical properties compared to the bulk ones. Among the nanoparticles that have received tremendous attention are cerium oxide nanoparticles.² Cerium (Ce) is considered the most abundant rare earth element. Cerium is more abundant in the earth compared to copper and tin.² Due to its high abundancy, cerium oxide (CeO_2) or usually called ceria³ is one of the rare earth oxide materials that has been widely studied and it has wide applications, such as catalysts^{3,4}, gas sensors (e.g. oxygen)⁵, solid oxide fuel cell (SOFC)⁶, UV protective coating⁷, corrosion protective coating⁸, bio-medicine^{2,9}, and particularly chemical-mechanical polishing (CMP) for the semiconductor industry.¹⁰ Ceria nanoparticle is well-known abrasive materials used for the chemical Mechanical Polishing (CMP) process for many years. This CMP is a very important process for all nanosized semiconductor devices. It was due to its superior removal selectivity and polishing efficiency of the oxide film.^{11,12} There are several methods that can be employed to synthesize ceria nanoparticles, e.g. precipitation, hydrothermal, green synthesis, microwave-assisted method, microemulsion, oxidation, and sonochemical.^{1,7,13,14,15} Among these methods, the precipitation method is considered one of the most promising methods and quite popular among researchers due to its simple process, inexpensive raw materials, controllable process, and the use of commonly available apparatus.^{14,15} There are numerous studies that reported the fabrication of ceria nanoparticles via the precipitation method. Oosthuizen, *et al.*¹⁶ reported about the preparation of ceria nanoparticles using different concentrations of ethanol (i.e. 10 – 50 mL) via a chemical precipitation process for gas sensing application. I-Tsan, *et al.*¹⁷ synthesized ceria nanoparticles via precipitation and annealed the produced ceria at different temperatures. They reported that the ceria produced had a cubic fluorite structure and the optimum annealing temperature of ceria

nanoparticles was above 500°C. Additionally, when increasing the temperature of calcination, i.e. 550°C to 1050°C, the size of the Ceria crystalline also increased from 8 to 75 nm. Anupriya, *et al.*¹⁸ also studied the production of ceria nanoparticles by a simple precipitation method for UV-blocking agents. They used cerium (III) nitrate hexahydrate as the cerium source, Cetyl trimethyl ammonium bromide as the surfactant, monoethanolamine as a reducing agent, and ethylene glycol/DI water mixture (1:1) as the solvent. They got ceria nanoparticles with an approximate size of 4 nm. They also suggested that the ceria nanoparticle could adsorb UV light quite well. To the best of our knowledge literature that studies the application of reflux condenser during the synthesis of ceria nanoparticles via the precipitation method is limited. Therefore, it is a good topic for research. In this study, cerium oxide (ceria) nanoparticles have been prepared via the precipitation method. A reflux condenser was used to help or maintain the temperature during the precipitation. The effects of three different ethanol/DI water ratios and post-heat treatment on the crystal structure and morphology of the ceria nanoparticles were studied.

EXPERIMENTAL

Material and Equipment

The precursor used to prepare ceria nanoparticles was cerium nitrate hexahydrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Whereas, ammonium solution NH_4OH (28-30%) was used as a precipitant. While the solvent was a mixture of ethanol (99%) and deionized (DI) water with different volumetric ratios (i.e. 1:1; 1:4; 0:1). All the chemicals were used without further purification. The apparatus used to synthesize ceria nanoparticles via precipitation was a three-neck flask equipped with a reflux condenser. The three-neck flask was put in the heating mantle with a stirrer and temperature controller. The purpose of the reflux condenser is to condense some vaporized ethanol, hence also maintaining the temperature inside the three-neck flask. Other equipments that were used for preparation and post-treatment of the samples are a glass beaker, pipette, magnetic stirrer, centrifuge, oven, and furnace. The centrifuge was used for the separation of the ceria precipitates from the solvent. While ovens and furnaces were used for drying and calcination of the samples, respectively.

Synthesis of Ceria

The ceria nanoparticles were synthesized via a precipitation at base condition. Figure-1 illustrates a schematic procedure of the ceria synthesis. Firstly, a mixture of ethanol/water was prepared at different volumetric ratios (1:1, 1:4, and 1:0) for about 20 mL. Then, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was poured into the solvent to make 0.2 M solution and mixed using a magnetic stirrer at room temperature for about 30 minutes. Afterward, the solution was poured into the three-neck flask apparatus and rigorously stirred using a heating mantle with a stirrer setup (see Fig.-1).

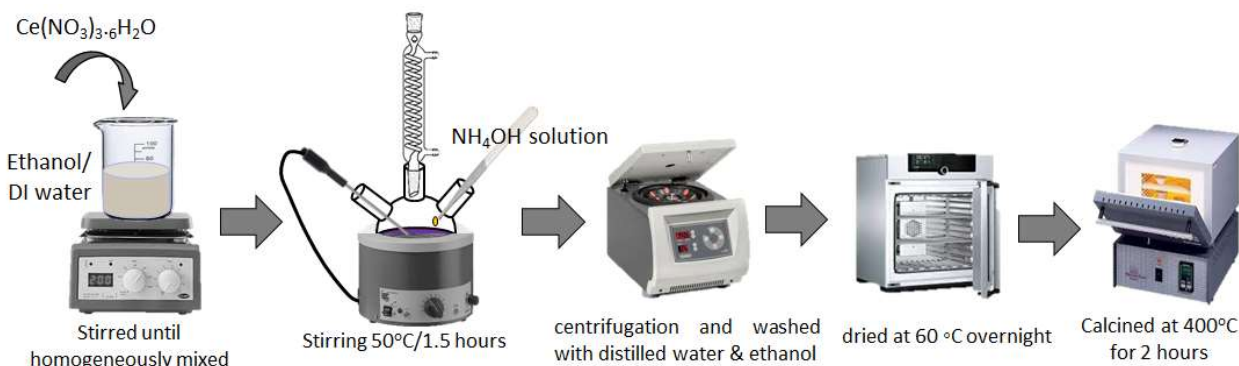
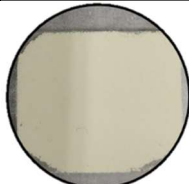


Fig.-1: Schematic Procedure for Synthesizing Ceria Nanoparticles

The temperature of the solution was maintained at 50°C by using a temperature controller and with the help of reflux condenser. After the temperature reached 50°C, about 1.7 mL of NH_4OH (28-30%) was added into the three-neck flask to precipitate ceria nanoparticles. The precipitation process was run for about 1.5 hours. When the NH_4OH solution was added, the mother solution became purple and subsequently became a pale yellow suspension. After the precipitation process is over (i.e. 1.5 hours), the yellow suspension was

put into a tube and then centrifuged to separate the precipitate. Afterward, the precipitate was thoroughly washed using DI water and then centrifuged again. The washing process was done three times, using DI water twice and using ethanol once. Afterward, the precipitate was put into an oven overnight for drying. Finally, some samples were put into a furnace for calcination at 400°C for 2 hours. Table 1 shows the sample nomenclature of ceria nanoparticles and their processing conditions. There are two variables, which are different ethanol/DI water ratio (i.e. 1:1; 1:4; 0:1) and post-heat treatments (i.e. drying only (D) and drying + calcination (C)).

Table-1: Sample Nomenclature of Ceria Nanoparticles and their Processing Conditions

Sample	Ceria-C1	Ceria-C2	Ceria-D2	Ceria-C3	Ceria-D3
Ethanol/DI water (ratio)	1:1	1:4	1:4	0:1	0:1
Powder appearance (color observation)					

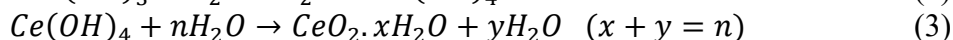
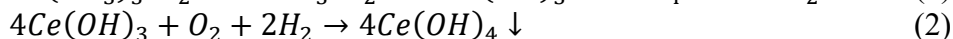
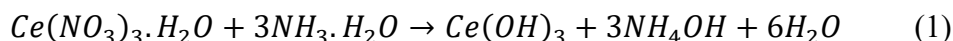
Note: The letters C and D denotes Calcination and drying post-heat treatment, respectively of ceria nanoparticles

Samples Characterization

The analysis of the ceria nanoparticles was done using an X-Ray Diffractometer (XRD) and Transmission Electron Microscopy (TEM) to study their crystal structure and morphology. The XRD analysis was conducted using the Rigaku XRD machine with Cu K α radiation (i.e. $\lambda = 1.5406 \text{ \AA}$). The XRD analysis conditions were as follows: room temperature, 2θ range of $10 - 80^\circ$, scan speed of 10 deg/min , and step size of 0.02° .

RESULTS AND DISCUSSION

The synthesis of ceria nanoparticles has been successfully conducted via the precipitation process. From the observation during the precipitation process. After the addition of ammonium solution, the solution mixture became purple. Afterward, after a couple of minutes, the purple solution subsequently turned into a yellow suspension. This yellow suspension indicated the formation of $\text{Ce}(\text{OH})_4$ precipitates.¹⁷ The precipitates were achieved by the addition of ammonium solution (NH_4OH) into the precursor ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) solution. The use of ammonium solution is to act as precipitating agent and base solution. In a solution with a high pH value, the Ce^{3+} is oxidized to Ce^{4+} and subsequently hydrolyzed into $\text{Ce}(\text{OH})_4$ and precipitated. However, $\text{Ce}(\text{OH})_3$ is also easily oxidized in air at room temperature and turned into $\text{Ce}(\text{OH})_4$ indicated by the appearance of a yellow suspension, which is a hydrous oxide, represented by $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$. Then $\text{Ce}(\text{OH})_4$ precipitates can be easily dehydrated into CeO_2 via heat treatment (i.e. drying, annealing).^{17,19} The complete course of a chemical reaction during the synthesis of CeO_2 via precipitation using ammonium solution as the precipitating agent can be described as follows.²⁰



After drying and calcination all the ceria samples powder resulted in yellow color, as shown in Table- 1. As noticed from the table, the yellow color of the ceria powder after drying only (i.e. Ceria-D2 and Ceria-D3) were a little bit different than the ceria powder after drying + calcination (i.e. Ceria-C1, Ceria-C2, Ceria-C3). The difference in color may be related to the size of the ceria nanoparticles.

Structural Analysis

The effect of the different volumetric ratios of ethanol/DI water (i.e. 1:0, 1:4, 0:1) and post-heat treatment (drying only and drying-calcination) on structural properties of ceria nanoparticles are investigated by using an X-Ray Diffraction (XRD) apparatus. Figure-2 shows the XRD pattern of the ceria nanoparticles. As seen in the Figure, all the XRD patterns of ceria nanoparticles samples are very similar to the standard XRD

pattern of the CeO_2 -cubic phase. All the XRD peaks are attributed to the 111; 200; 220; 311; 222; 400; 331; 420; and 422 planes. These planes can be associated with the face-centered cubic lattice structure of CeO_2 .¹¹ As seen in the figure, no other impurities like cerium nitrate were detected in the XRD pattern. To further analyze the structural properties of the prepared ceria nanoparticles, the highest intensity peak of the XRD pattern (at $2\text{-theta} = 28.6^\circ$) for different ceria nanoparticles (based on Fig.-2) was compared and plotted in Fig.-3a. The XRD peaks of the ceria samples can exhibit the crystalline nature of the samples. As seen in the figure the intensity peak of the XRD pattern for all the ceria nanoparticles samples after calcination was higher than the ones with drying treatment only. This result is expected and in accordance with the literature. Kuncham, *et al.*²¹ reported that with the increase in temperature of heat treatment (i.e. calcination) the intensity of the peak increased, while the peak wide decreased, which was due to better crystallization. A similar result has also been reported by other literatures.¹⁵

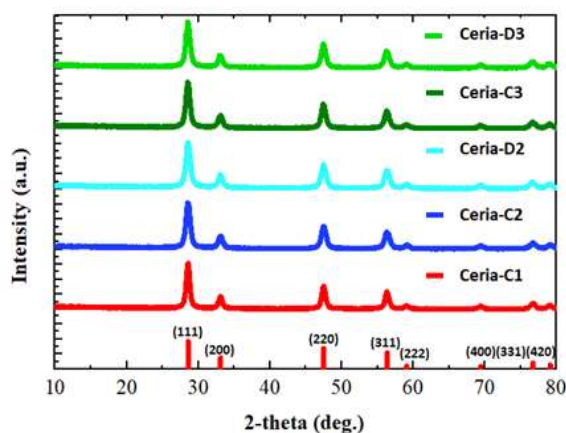


Fig.-2: XRD Spectrum of Ceria Samples Powder

The average size of the ceria crystallite was also determined from the XRD pattern using the well-known Scherrer's equation:²²

$$FWHM = (0.9 \times \lambda) / (D \times \cos(\theta))$$

Where FWHM is the Full Width at Half-Maximum of the XRD peak (rad.), 0.9 is the k value (i.e. shape factor), λ is the x-ray wavelength ($\lambda = 1.5406 \text{ \AA}$), D is the average size of the CeO_2 crystallite (nm), θ is the Bragg angle (rad.). It was found that the average crystallite size of the ceria nanoparticles for Ceria-C1, Ceria-C2, and Ceria-D2, Ceria-C3, Ceria-D3 were about 14, 11.3, 11.0, 11.6, 11.5 nm, respectively and are plotted in Fig.-3b. As noticed, CeO_2 nanoparticles prepared by ethanol/DI water ratio of 1:1 (i.e. Ceria-C1) had the biggest average crystallite size.

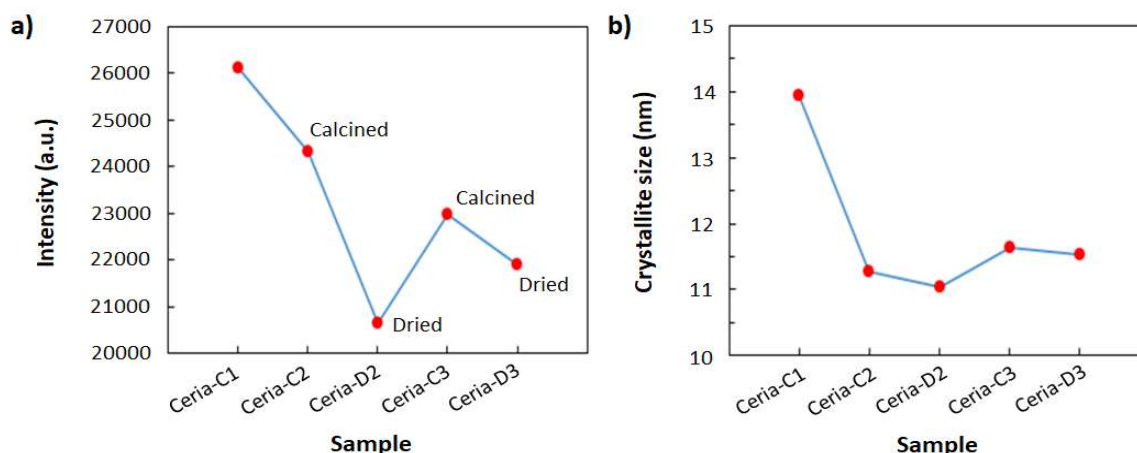


Fig.-3: Comparison of a) Highest Intensity Peak of the XRD Pattern and b) Crystallite Size for Different Ceria Nanoparticles (based on the XRD pattern in Fig.-2)

Morphological Analysis

A Transmission Electron Microscopy (TEM) analysis was conducted to investigate the morphology of the ceria nanoparticles. The TEM images of ceria nanoparticles are shown in Fig.-4. As noticed, the TEM image of ceria nanoparticles prepared using ethanol/DI water ratio of 1:1 (i.e. Ceria-C1) shows better morphology compared to others. The Ceria-C1 sample exhibited sphere-like nanoparticles (indicated by the red arrows in Fig.-4a). On the other hand, the other ceria samples showed much more agglomerated nanoparticles.

Dispersion Stability Analysis

As previously mentioned in the introduction, one of the important applications of CeO_2 nanoparticles is for Chemical Mechanical Polishing (CMP) which has been widely used in semiconductor industries. Therefore a dispersion stability analysis is quite important. To study the dispersion stability, firstly the ceria powder was put in 10 mL of a vial filled with DI water and sonicated for about 6 minutes and then left for a couple of days.

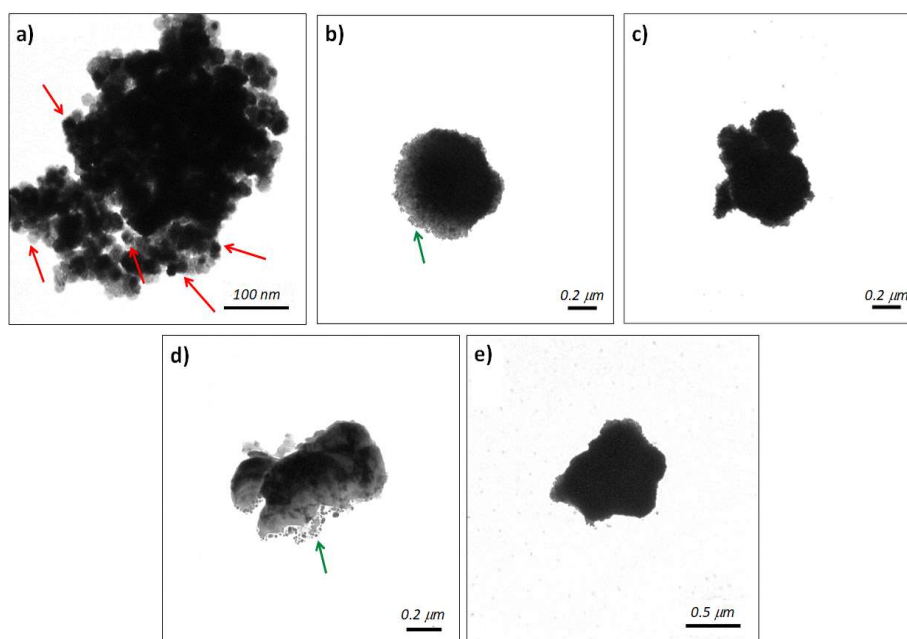


Fig.-4: TEM Images of CeO_2 Nanoparticles Prepared By Precipitation Method: a) Ceria-C1; b) Ceria-C2; c) Ceria-D2; d) Ceria-C3; e) Ceria-D3

The appearances of the ceria powder dispersed in DI water before and after 5 days are exhibited in Fig.-5. It can be observed that most of the ceria samples showed similar dispersion stability levels, which was not quite good. There was a change in the color of the suspension, which implies that some of the ceria nanoparticles have settled down. Nevertheless, as seen in the figure, the suspension of Ceria-C1 shows a little bit better dispersion compared to the others. This finding is in accordance with the fact that the TEM image of Ceria-C1 also showed better dispersion and morphology of ceria nanoparticles.

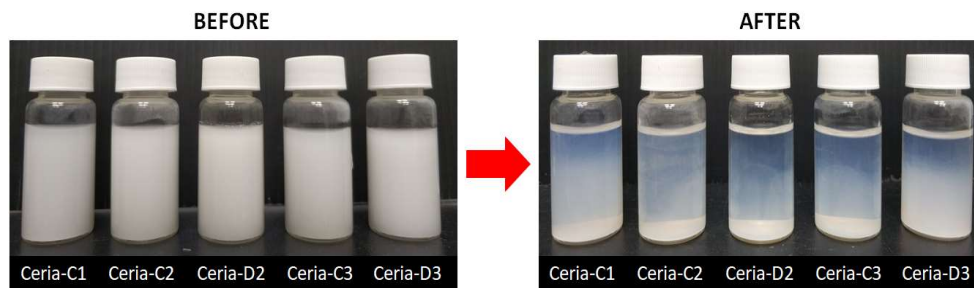


Fig.-5: Appearance of the Ceria Nanoparticles Suspensions after a Couple of Days

CONCLUSION

In this study, the synthesis of cerium oxide (CeO_2) or ceria nanoparticles has been conducted via a simple precipitation method. The precipitation process was done in a three-neck flask with a reflux condenser. The ceria nanoparticles were synthesized using three different ethanol/DI water ratios (i.e. 1:1; 1:4; 0:1) and different post-heat treatments (i.e. drying only and drying + calcination). The effects of these two variables on the morphology and crystal structure of the ceria nanoparticles were studied using TEM and XRD, respectively. The XRD results revealed that the intensity peak of the XRD pattern (at $2\text{-}\theta = 28.6^\circ$) for all the ceria nanoparticles samples after drying + calcination was higher than the ones with drying treatment only. Moreover, the average crystallite size of the ceria nanoparticles for Ceria-C1, Ceria-C2, and Ceria-D2, Ceria-C3, Ceria-D3 were about 14, 11.3, 11.0, 11.6, and 11.5 nm, respectively. As noticed, the average crystallite size of the CeO_2 nanoparticles prepared using the ethanol/DI water ratio of 1:1 (i.e. Ceria-C1) had the biggest crystallite size. Nevertheless, the TEM images showed that Ceria-C1 showed better morphology and dispersion compared to the others. The Ceria-C1 sample also clearly exhibited a sphere-like nanoparticles. In the other hand, the other ceria samples showed much more agglomerated nanoparticles. This finding can be related to the dispersion stability analysis, which showed that the suspension of Ceria-C1 shows a little bit better dispersion compared to other ceria samples.

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