

Room Temperature Synthesis of Nano Crystalline Cerium Oxide Using Hydrazine and Ammonia

Noriya IZU, Toshio ITOU, Woosuck SHIN, Ichiro MATSUBARA and Norimitsu MURAYAMA*

National Institute of Advanced Industrial Science and Technology (AIST), Advanced Manufacturing Research Institute, 2266-98, Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya-shi 463-8560

*National Institute of Advanced Industrial Science and Technology (AIST), Planning Headquarters, AIST Tsukuba Central 2, 1-1-1, Umezono, Tsukuba-shi 305-8568

ヒドラジン又はアンモニアを使ったナノ結晶酸化セリウムの室温合成

伊豆典哉・伊藤敏雄・申 ウソク・松原一郎・村山宣光*

産業技術総合研究所先進製造プロセス研究部門, 463-8560 名古屋市守山区下志段味穴ヶ洞 2266-98

*産業技術総合研究所企画本部, 305-8568 つくば市梅園 1-1-1 つくば中央第 2

The synthesis of nano crystalline particles of cerium oxide at room temperature was investigated in detail. Highly crystallized cerium oxide nano powder with a particle size of 10 nm was obtained by adding a hydrazine aqueous solution or an ammonia aqueous solution into a cerium nitrate solution followed by stirring the mixed solutions over a prolonged period at room temperature. It was considered that the good crystallinity was attributable to the use of an aqueous solution containing Ce(III) ions as a starting solution.

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1. Introduction

Nano powder of cerium oxide has many uses, for example, as a promoter in a three-way catalyst, the sensing material for oxygen sensors, and as a material used in chemical mechanical polishing (CMP). There are some reports concerning the synthesis of cerium oxide nano powder.^{1)–6)} In many cases, a heating process is included in the synthesis. At the same time, synthesis around room temperature has been reported by some researchers.^{7)–9)} The merits of room temperature synthesis are that very small particles can be obtained because there is no aggregation of particles.

Zhang et al. have synthesized nano crystals of cerium oxide at room temperature by mixing hexamethylenetetramine (HMT) with a cerium nitrite solution.^{7),8)} Manorama et al. have synthesized nano particles of cerium oxide around room temperature by mixing hydrazine with a cerium nitrite solution and used the nano particles as the sensing material for oxygen sensors.¹⁰⁾ In the Manorama et al. report, the sensing properties have been investigated and reported, but the detail of the room temperature synthesis of the cerium oxide nano particles was not reported.

In this study, we investigated the synthesis of nano particles of cerium oxide at room temperature by using hydrazine as well as ammonia.

2. Experimental

40 cm³ of a 0.4 kmol/m³ hydrazine (NH₂NH₂) aqueous solution was slowly added to 100 cm³ of a 0.05 kmol/m³ cerium nitrate (Ce(NO₃)₃) aqueous solution at the rate of about 2 cm³/min. The cerium nitrate solution was colorless before adding the hydrazine aqueous solution. After adding 1 or 2 cm³ of the hydrazine aqueous solution, the color of the solution changed to pale red. After adding 8 cm³, a precipitate appeared in the solution and the solution became cloudy. After adding 10 cm³, the color of the precipitate changed to reddish-purple or brown. Immediately after adding 40 cm³ of

the hydrazine solution, the pH value of the solution was about 9. The solution was stirred for 18 to 24 h due to the very slow reaction rate. After stirring for this prolonged period, the color of the precipitate finally changed to pale yellow and the pH value of the solution changed to 7. The precipitate was separated from the solution by decantation or centrifuging.

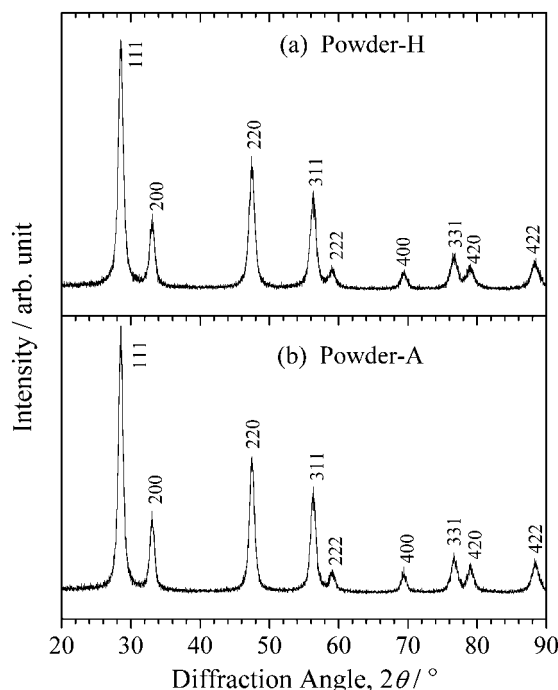


Fig. 1. XRD patterns for the powders dried at 50°C. (a) Powder-H, prepared using hydrazine, (b) Powder-A, prepared using ammonia.

All the processes were carried out at room temperature until the separation. The precipitate was dried in vacuum oven at 50°C or room temperature to obtain a dried powder.

We also carried out the same experiment using a 0.4 kmol/m³ ammonia (NH₃) aqueous solution instead of the hydrazine aqueous solution. The change of color and pH value was almost the same as the experiment using the hydrazine aqueous solution. The powders prepared using the hydrazine and the ammonia were called "Powder-H" and "Powder-A," respectively. The powders obtained were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

A similar experiment was then carried out using cerium ammonium nitrate (NH₄)₂Ce(NO₃)₆ as a replacement for the cerium nitrate. In the cerium ammonium nitrate aqueous solution, the valence of the Ce ion is IV. 40 cm³ of a 0.4 kmol/m³ ammonia aqueous solution were added to 100 cm³ of a 0.05 kmol/m³ cerium ammonium nitrate aqueous solution. When the ammonia aqueous solution was added slowly, sometimes the precipitate did not form at all, and sometimes the precipitate dissolved when the solution was stirred over a prolonged period. Therefore, the ammonia aqueous solution

of 50 cm³ was added quickly and then the precipitate obtained was filtered and dried at 70°C in air. The powder obtained in this process was called "Powder-E"

3. Results and discussion

XRD patterns for the powders dried at 50°C are shown in Fig. 1. The XRD pattern for Powder-H was quite similar to that for Powder-A. Both patterns showed a cubic fluorite structure. Therefore, after drying at 50°C it was confirmed that the powders were cerium oxide. The calculation of the crystallite size of the powders from the full width at half maximum of the peaks using the Hall method revealed that the crystallite size was 11 nm, and the strain was about 0.3% for both Powder-H and Powder-A. These results indicated that cerium oxide in the powders was not amorphous but crystalline with good crystallinity.

TEM images of the powders dried at 50°C are shown in Fig. 2. The TEM samples were prepared by ultrasonic dispersion of the powders. Crystallites of around 10 nm were observed in both Powder-H and Powder-A. These results were consistent with the crystallite size calculated from the XRD patterns.

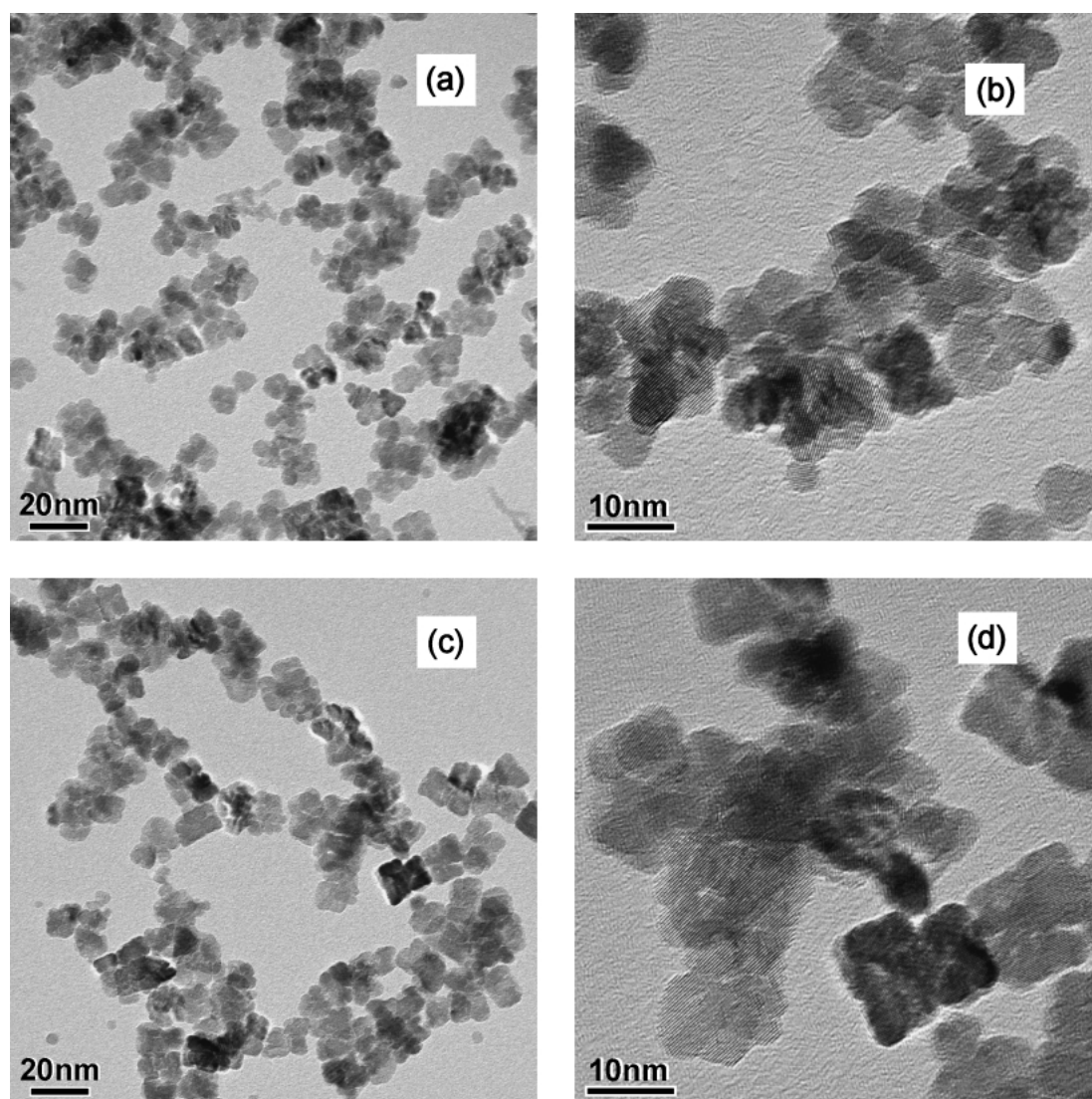


Fig. 2. TEM images of the powders dried at 50°C.

(a) and (b) Powder-H, prepared using hydrazine, (c) and (d) Powder-A, prepared using ammonia.

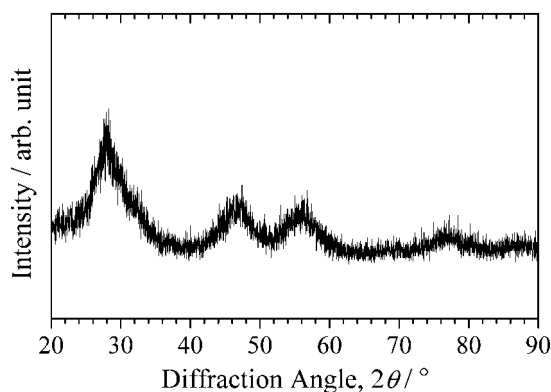


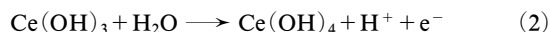
Fig. 3. XRD pattern for Powder-E, prepared from cerium ammonium nitrate.

The XRD patterns for Powder-H and Powder-A obtained after drying at room temperature in a vacuum were exactly the same as those shown in Fig. 1. Therefore, it was confirmed that cerium oxide nano powder with good crystallinity was able to be obtained even when the entire synthesis process was carried out at room temperature.

Here we discuss the mechanism of the cerium oxide synthesis. By adding hydrazine aqueous solution or ammonium aqueous solution to cerium nitrate solution, the following reaction occurred:



As $\text{Ce}(\text{OH})_3$ is unstable in air,¹¹⁾ it was considered that $\text{Ce}(\text{OH})_3$ changed to $\text{Ce}(\text{OH})_4$ by oxidation during the prolonged stirring. If this change is described by the following reaction, it can be seen that protons are generated:



The change of the pH value from 9 to 7 could be attributed to H^+ in Reaction (2). According to Chen, P.-L. and Chen, I.-W., the color of CeO_2 was pale yellow and the precursor of the CeO_2 was pinkish-purple.²⁾ The color change observed in this study was consistent with the aforementioned report. The crystallinity is described in detail later.

The XRD pattern for Powder-E is shown in Fig. 3. The diffraction peaks were very broad so that Powder-E was almost amorphous. Therefore, in the case of synthesis at around room temperature, it became clear that cerium oxide nano powder with good crystallinity could be obtained from

$\text{Ce}(\text{NO}_3)_3$.

Next we will discuss the difference of crystallinity between Powder-E and Powder-H (or Powder-A). In the case of powder-H (or powder-A), two reactions (Reactions (1) and (2)) occur to form the cerium oxide. As described above, the rate of Reaction (1) is high, while the rate of Reaction (2) is low. Although the particles formed in Reaction (1) were amorphous, crystallinity could be improved in Reaction (2) because of its slower rate. In the case of Powder-E, the following reaction occurs:



Reaction (4) is very fast, like Reaction (1). Therefore, the amorphous state of Powder-E seems to be attributable to the high rate of Reaction (4). From the above discussion, it was considered that Reaction (2) contributed to improving the crystallinity of the cerium oxide nano particles.

4. Conclusion

Cerium oxide nano powder with good crystalline particles of 10 nm was obtained by mixing hydrazine aqueous solution or ammonia aqueous solution with cerium nitrate solution and stirring the mixed solutions over a prolonged period at room temperature. It was considered that the good crystallinity was attributable to the use of an aqueous solution that contained $\text{Ce}(\text{III})$ ions as a starting solution.

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