# Synthesis of cerium oxide nanoparticles by hydrothermal crystallization with citric acid

T. MASUI, H. HIRAI, N. IMANAKA*, G. ADACHI
*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*
E-mail: imanaka@chem.eng.osaka-u.ac.jp

T. SAKATA, H. MORI
*Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki, Osaka 567-0047, Japan*

Cerium oxide (ceria) is an important material for the application to practically used polishing agents [1], sunscreens [2], solid electrolytes [3], and automotive exhaust catalysts [4]. Recently, ultrafine nanoparticles have attracted much attention due to the physical and chemical properties that are significantly different from those of bulk materials. Many studies have been carried out to obtain ceria single nanoparticles smaller than 10 nm [5].

The method described here is based on a hydrothermal synthesis. Ceria nanoparticles have already been synthesized by the conventional hydrothermal methods, and employing tetravalent cerium salts ($Ce(SO_4)_2$, $Ce(NH_4)_4(SO_4)_2$, and $(NH_4)_2Ce(NO_3)_6$) as starting materials is very effective to obtain ultrafine ceria particles smaller than 5 nm [6–9]. However, in these processes, it is difficult to obtain well-dispersed particles because agglomeration and subsequent precipitation occurred as soon as the particles formed due to the high surface energy of the nanoparticles. In addition, the presence of $SO_4^{2-}$ ions in a solution accelerates the agglomeration of the particles [9]. On the other hand, a transparent colloidal solution of 2 nm ceria particles has been prepared by the reaction of cerium metal in 2-methoxyethanol [10]. However, agglomerated yellow precipitates of which the crystallite size was >100 nm were obtained as well as a dark brown transparent solution of 2 nm ceria particles, and also the starting cerium metal is too expensive for practical use. In this study, therefore, a new method based on a hydrothermal process was applied to obtain not only ultrafine but also well-dispersed nanoparticles by the application of citric acid as a protective agent against particle growth.

A mixture of 1.0 M aqueous solutions of cerium chloride and citric acid was added to an excess amount of 3.0 M ammonia water. The molar ratio of cerium chloride and citric acid was 1 : 1. After stirring for 24 h at 323 K, a dark brown transparent liquid was obtained. Then the transparent solution was transferred into a Teflon bottle in a vessel and heated at 353 K for 24 h to well crystallize the produced particles. Although the apparent status of the liquid did not change by the heat treatment, the crystallinity after the treatment became higher than before. The brown liquid showed the Tyndall effect, an indication that it contains well-dispersed colloidal particles. The particles were forcibly separated by centrifuging in a relative centrifugal field of $4.1 \times 10^4$ g ($2.1 \times 10^4$ rpm) for 24 h. After successive washing with deionized water and methanol by ultrasonic agitation, the forcibly centrifuged particles were dried by a freeze-drying method.

The X-ray powder diffraction pattern of the ultrafine powders obtained in this study showed characteristic peaks of cerium(IV) oxide and the width of the peaks was broad because of their small particle size. Fig. 1 shows the electron diffraction pattern of the obtained particles, and the Debye-Scherrer rings were consistently indexed as those of cubic cerium(IV) oxide with the fluorite structure [11].

Fig. 2 shows a high-resolution transmission electron microscopic (HREM) image of the synthesized ultrafine cerium(IV) oxide particles recorded using a Hitachi H-9000 microscope operating at 300 kV. Samples were prepared by dipping a microgrid into the dark brown transparent solution followed by drying in air. The particle size was very small, although the particles somewhat agglomerate with each other. The HREM image also showed well-defined crystallites and their lattice images for all particles. Crossed lattice fringes corresponding to the {111} reflections ($0.31_2$ nm) were clearly observed. The B.E.T. specific surface area of the powders was 211 $m^2 \cdot g^{-1}$. Assuming that all particles were spheres, their size calculated from the B.E.T. specific surface area was 3.9 nm, which was in good agreement with that observed from the HREM image. These results clearly show the evidence for weak agglomeration of the particles.

In the present synthesis, citric acid works as a protective agent against particle growth. Fig. 3 shows the FTIR spectrum of the obtained ceria nanoparticle. Three strong absorption peaks were observed at 3500, 1560, and 1402 $cm^{-1}$. The former was attributed to the stretching band of the hydroxyl group and the others were attributed to the antisymmetric and symmetric stretching band of the carboxyl group, respectively. As seen in Fig. 3, it can be considered that the surface of the ceria nanoparticles was homogeneously covered with citric acid molecules. Consequently, growth

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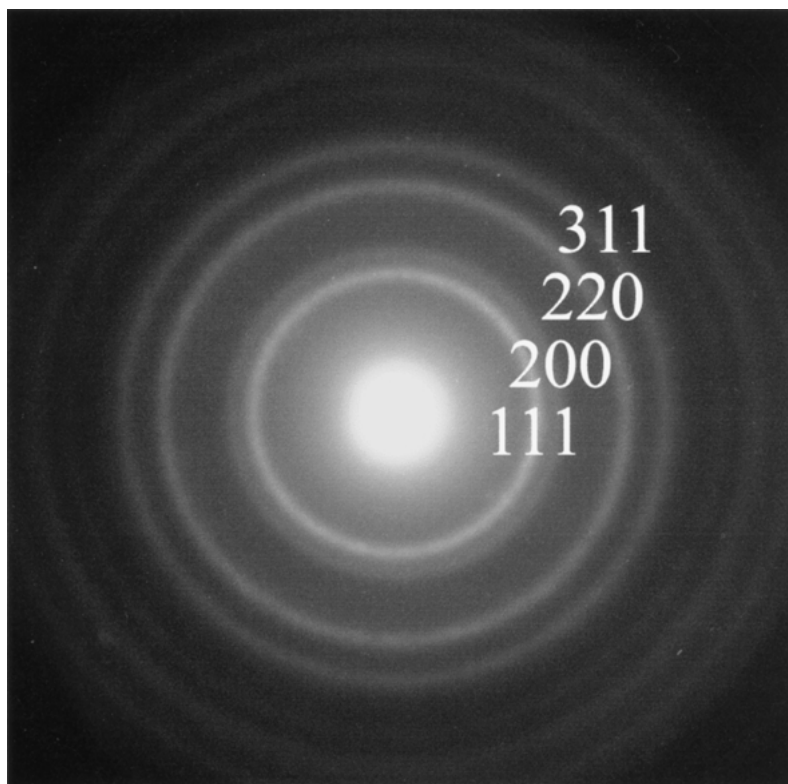*Author to whom all correspondence should be addressed.

*Figure 1* Electron diffraction pattern of the particles collected from the colloidal solution prepared under a hydrothermal condition at 353 K in the presence of citric acid.

of the particles was inhibited and well-dispersed ceria nanoparticles were prepared as aimed.

Some references on the hydrothermal synthesis of ceria suggest that the promotion of smaller ceria nanoparticles from $Ce^{4+}$ solution was due to the difference in the nucleation number of hydrated $Ce^{4+}$ ions in the solutions [7, 8]. That is, in the case of Ce(III) salt, the oxidation process from $Ce^{3+}$ to $Ce^{4+}$ are necessary and, therefore, the rate and the number of nucleation of the hydroxide from the Ce(III) salt became
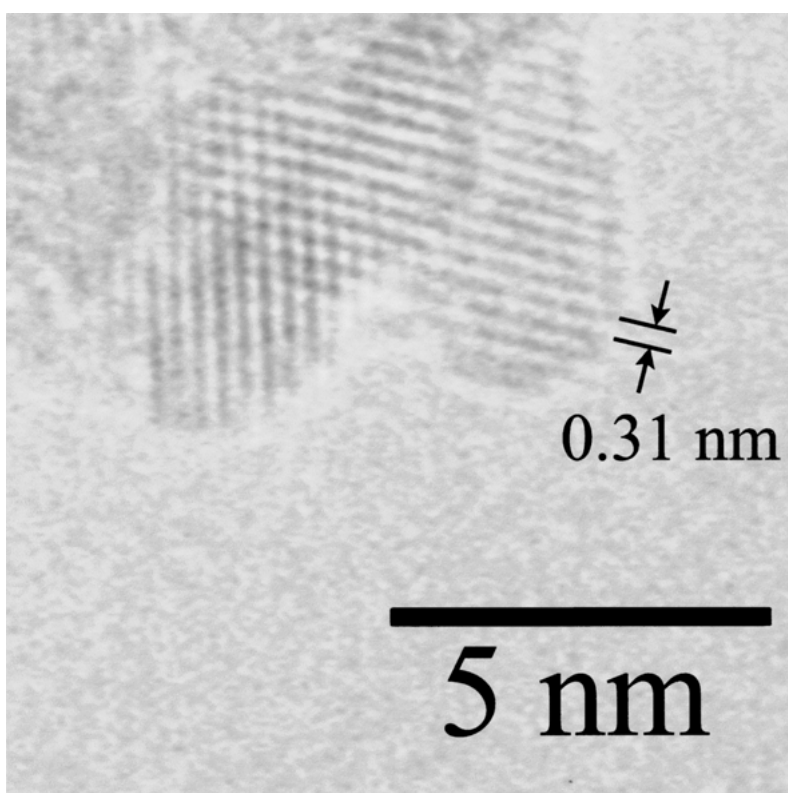


*Figure 2* HREM photograph of $CeO_2$ nanoparticles prepared under the hydrothermal condition at 353 K in the presence of citric acid.
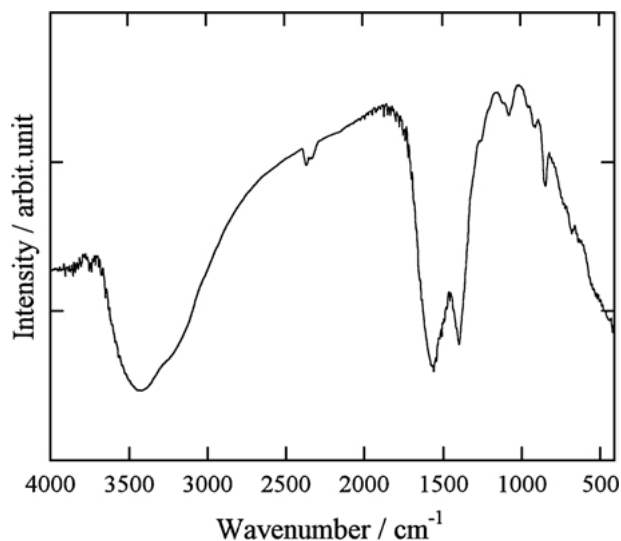
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*Figure 3* FTIR spectrum of the CeO$_2$ nanopowder prepared under the hydrothermal condition at 353 K in the presence of citric acid.

slower and fewer than those from the Ce(IV) salt. As a result, the very fine precursors for the final oxide are prepared in the case of Ce(IV) salts, where the starting precursor from Ce(III) salts consists of relatively large particles before the hydrothermal treatment. As mentioned above, however, agglomeration and precipitation would take place due to the highly active surface of the nanoparticles even in the case of using Ce(IV) salts when the surface is not protected.

On the contrary, in the present method the final size of the cerium oxide particles is restricted by the adsorption of citric acid molecules on the surface of the particles formed, despite the fact that the mechanism of the ceria formation are similar to the conventional hydrothermal crystallization using Ce(III) salts. When the aqueous solution of cerium chloride are mixed with citric acid, stable cerium-citric acid complexes are formed in the solution [12]. The hydrolysis of the complexes produces colloidal sol in which the cerium hydroxide nanoparticles covered with citric acid, and these molecules adsorbed on the surface of the particles protect them against the further particle growth. During the hydrothermal crystallization in the sealed vessel, the citric acid molecules remain on the surface of the particles. Therefore, very small ceria particles under 5 nm without agglomeration were successfully realized even if Ce(III) salts were employed as starting materials.

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