Transparent colloidal solution of 2 nm ceria particles

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The reaction of cerium metal in 2-methoxyethanol at 200–250 °C yielded a transparent colloidal solution of ultrafine (2 nm size) ceria particles.

Hydrothermal oxidation of metals has been widely examined as a synthesis route for inorganic materials and various compounds having specific properties have been prepared.[1,2] Although it is known that some metals corrode in alcohols, oxidation of metals in alcohols has never been examined from the viewpoint of material synthesis until our recent report that the reaction of aluminium metal in alcohols at 250–300 °C yielded alkoxyalumoxanes.[3] As an extension, we applied this method to cerium metal and found that a transparent colloidal solution of ultrafine ceria particles was directly obtained by the reaction of cerium metal in 2-methoxyethanol at 200–300 °C.

Cerium metal chips [*ca.* 2.40 g; 0.2 mm × 3.5 mm × (3–5) mm] and 2-methoxyethanol (85 mL) were placed in a test tube, which was then set in an autoclave (200 mL). An additional 20 mL of 2-methoxyethanol was placed in the gap between the test tube and the autoclave wall. The autoclave was completely purged with nitrogen and heated to 250 °C at a rate of 2.3 °C min^{-1} and kept at that temperature for 2 h. After the assembly was cooled, the product mixture was centrifuged and yellow precipitates and a dark brown transparent solution were obtained. The XRD pattern of the precipitates showed characteristic peaks of ceria, and the crystallite size of the precipitates, calculated by the X-ray diffraction (XRD) line broadening technique, was > 100 nm. The precipitates are postulated to derive from the ceria surface layer of the cerium metal chips, because the properties of the precipitates were not altered by the reaction conditions.

Addition of distilled water to the transparent solution obtained as the supernatant after centrifugation of the product did not lead to any change except for dilution of the color of the solution. When the solution was kept standing for several weeks with gradual evaporation of the solvent, gelation took place liberating a small amount of a colorless supernatant, and the gel gradually shrank while remaining transparent. On the other hand, when the solution was kept in a closed bottle, it was stable for at least several months. Addition of salt solutions such as aqueous NaCl to the transparent solution immediately caused the formation of gelatinous precipitates.

Transmission electron microscopic observation of a specimen prepared by dipping a microgrid into the diluted solution followed by drying in air revealed that ultrafine particles of size 1.5–2 nm formed a thin film on the microgrid, which is believed to arise from agglomeration at the drying stage owing to the large surface energy of the particles. Electron diffraction of the film gave diffuse 111, 200, 220, 311 Debye–Scherrer rings of cubic ceria with the fluorite structure.[4] These results indicate that the dark brown transparent solution is a colloidal solution of ultrafine particles of ceria.

The colloidal particles were coagulated by addition of methanol and aqueous NH_3 to the colloidal solution. The use of NaCl solution was avoided because of possible effects of the remaining salt on the properties of the particles. The precipitates were separated from a slightly turbid supernatant by centrifugation, washed with methanol, and then air-dried. The yellow powder obtained exhibited fairly broad XRD peaks (Fig. 1);

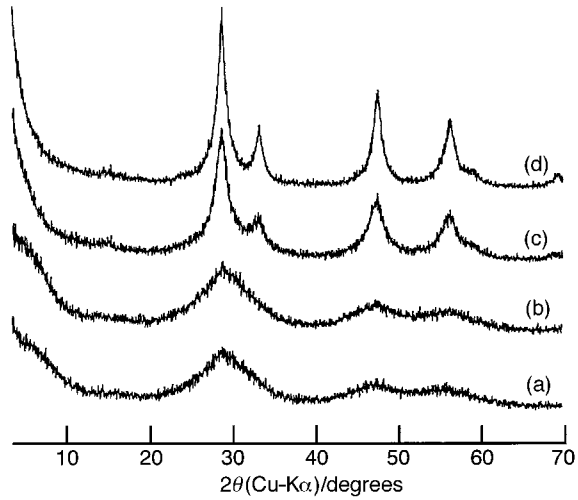

Fig. 1 XRD patterns of the powders collected from the colloidal solutions prepared by the reaction of cerium metal in 2-methoxyethanol at: (a) 200, (b) 250, (c) 280 and (d) 300 °C.

however, the peak positions were identical to the three strongest lines for cubic ceria. The crystallite size of the powder was calculated to be *ca.* 2 nm, which was essentially identical with the particle size observed by TEM, suggesting that each particle observed by TEM is a single crystal of ceria.

Various methods have been reported for the synthesis of ultrafine ceria particles.[5–13] However, as far as we are aware, the smallest particle size of ceria prepared so far is 2.6 nm, prepared by Masui *et al.*[12] using reversed micelles. Note that the reduction of particle size from 2.6 to 2 nm corresponds to the reduction of number of cerium atoms in a particle by a half and

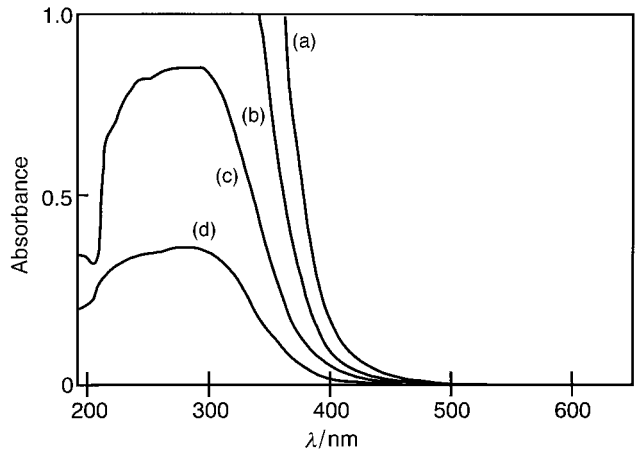

Fig. 2 Electronic spectra of the colloidal solution of ultrafine ceria particles. The original colloidal solution was obtained by the reaction of cerium metal in 2-methoxyethanol at 250 °C for 2 h, and the solution was diluted with 2-methoxyethanol to a concentration of (a) 0.172, (b) 0.086, (c) 0.043 and (d) 0.017 g L^{-1}.

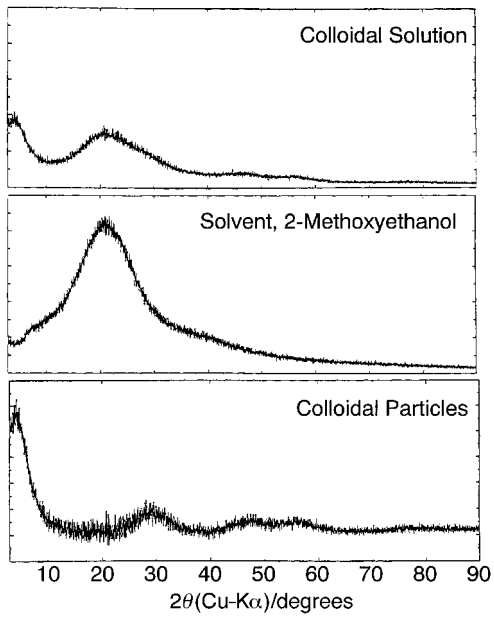

Fig. 3 XRD pattern of the ceria colloidal particles in the transparent solution (bottom) calculated by subtraction of the XRD pattern of the solvent, 2-methoxyethanol, (middle) from that of the colloidal solution (top). The XRD patterns were recorded on a Rigaku Rint-Ultima$^+$ diffractometer equipped with a θ–θ goniometer.

that a spherical ceria particle with a diameter of 2 nm contains only 100 cerium atoms.

The reaction proceeded at as low as 200 °C yielding a transparent solution, but the particle size of the ceria colloid was not decreased (Fig. 1). On the other hand, increase in the reaction temperature above 250 °C progressively increased the crystallite size of the ceria particles (8 nm by the reaction at 300 °C).

When the particles were calcined, the XRD peaks gradually sharpened, but no phases other than ceria were detected in the calcined samples. Crystal growth took place after calcination at 450 °C, *i.e.* at a much lower temperature than the lowest crystal growth temperature of 'reactive' 15.5 nm ceria powders prepared by the hydrazine method.[11]

Electronic spectra of the diluted colloidal solutions (Fig. 2) exhibited a strong absorption band at the UV region, whereas no absorption was detected above 500 nm. The observed absorbance followed Lambert–Beer's law, suggesting that the ultrafine ceria particles are well dispersed with no evidence for agglomeration under the concentrations of the UV measurement. The bandgap energies, E_i and E_d, for the ceria particles were calculated from these spectra to be 2.90 and 3.52 eV (1 eV $= 1.602 \times 10^{-19}$ J), respectively. These values were larger than those reported for the 2.6 nm ceria particles,[12] owing to the quantum size effect, although slightly larger values have been reported for ceria films.[14–16]

To ensure that the ultrafine ceria particles were not originated by any stages of the work-up process, XRD of the colloidal solutions was examined (Fig. 3). The XRD patterns of the colloidal particles, calculated by subtracting the XRD pattern of the solvent, 2-methoxyethanol, from that of the colloidal solutions, coincided with those for the particles obtained after coagulation. Therefore, it was concluded that the ultrafine ceria particles are actually present in the solution.

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