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Preparation of monodispersed nanocrystalline CeO_2 powders by microwave irradiation

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Monodispersed nanocrystalline CeO_2 powders of size *ca.* 2.0 nm displaying quantum size effects have been prepared by microwave irradiation in an aqueous solution containing $(NH_4)_2Ce(NO_3)_6$, PEG and NaAc.

Ceria (CeO_2) is a rare earth oxide with a high refractive index and a very sharp fundamental absorption edge and is a semiconductor with a band gap of 3.2 eV. It is also a highly efficient UV absorber and is used as an additive to glass (2–4% CeO_2) to protect light-sensitive materials, as a coating for corrosion protection of metals, as an oxidation catalyst, and as a counter electrode for electrochromic devices[1] as proposed recently. It is currently also being used as an oxygen ion conductor in solid oxide fuel cells (SOFCs), electrolyzers, oxygen pumps and amperometric oxygen monitors owing to its high oxygen ion conductivity.[2] Many studies have been conducted to prepare fine CeO_2 powders by using urea-based homogeneous precipitation,[3] hexamethylenetetramine-based homogeneous precipitation,[4] hydrothermal synthesis,[2] or cathodic electrogeneration of base.[5] Transparent colloidal solutions of ultrafine ceria particles were also directly obtained by Masashi *et al*,[6] by the reaction of cerium metal in 2-methoxyethanol at 200–300 °C. However, the preparation of nanocrystalline CeO_2 is very difficult using conventional conditions, and it is thus a challenge to find a novel approach to prepare the nanocrystalline oxide.

Since 1986, microwave irradiation has found a number of applications as a heating method in chemistry. As a quick, simple and energy efficient method, microwave synthesis has been developed, and is widely used for the synthesis of zeolites and ceramic materials.[7–11] Compared with conventional methods, microwave synthesis has the advantages of very short reaction times, production of small particles with a narrow particle size distribution, and high purity. Jansen *et al.* suggested that these advantages could be attributed to fast homogeneous nucleation and ready dissolution of the gel.[7] Unfortunately the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat uncertain and speculative. However, it is well known that the interaction between dielectric materials, liquids or solids, and the microwaves leads to what is generally known as dielectric heating in which electric dipoles in such materials respond to the applied electric field. In liquids, this constant reorientation leads to a friction between the molecules, which subsequently generates heat.[12] Many microwave phenomena are poorly understood such as non-thermal effects and the superheating effect.[2,13] In this study, a novel method for the preparation of ultrafine nanocrystalline cerium oxide is reported. Monodispersed nanocrystalline CeO_2 powders were successfully prepared by microwave irradiation by means of hydrolysis of $(NH_4)_2Ce(NO_3)_6$ in an aqueous solution containing poly(ethylene glycol)-2000 (PEG) and NaAc. Analysis of the results showed that the resulting CeO_2 powders were well crystallized, of *ca.* 2 nm size and showing a large quantum size effect.

An aqueous solution of 1 wt% PEG, 0.01 mol L^{-1} $(NH_4)_2Ce(NO_3)_6$ and 1 wt% NaAc was exposed to microwave radiation at a power level of 30% (the microwave operating in a 30 second cycles, on for 9 s, and off for 21 s at a total power of 650 W for 10 min), and then cooled to room temperature.‡ The resulting precipitate was centrifuged, washed with distilled water and dried in air. The final yellow product was collected for characterization.

The obtained powders were characterized by X-ray powder diffraction (XRD) (Fig. 1). The XRD pattern of the as-prepared product showed the presence of broad peaks, which corresponded to the (111), (220), (311) planes for a cubic fluorite structure.[14] The broadness of the peaks indicated that the crystallite size was very small. The microstructure of the sample was examined by high-resolution transmission electron microscopy (HRTEM). Typical TEM and HRTEM images of the sample are shown in Fig. 2(a) and (b). It is clear that as-prepared CeO_2 powders are crystalline with *ca.* 2 nm particle size (HRTEM image). In addition monodispersed nanocrystals were observed.

The UV–VIS absorption spectrum of the product dispersed in toluene is shown in Fig. 3 and shows a very large shift compared with the pure bulk crystal. The band gap E_g was 4.25 eV as calculated by the direct conversion method (in Fig. 4).[15] This is 1.0 eV larger than that of the pure bulk crystal ($E_g = 3.19$ eV).[1] The increase in the magnitude of the band gap is a consequence of the quantum size effect.

The proposed mechanism of microwave heating hydrolysis synthesis of CeO_2 nanoparticles may be as follows: first, hydrated Ce^{4+} ions can form complexes with H_2O molecules or OH^- ions. Polymers of this hydroxide, $Ce(H_2O)_x(OH^-)_y{}^{(4-y)+}$, can then serve as the precursors of the oxide. The starting precipitate from the Ce(IV) salt may be formed by nucleation of hydrated $Ce(H_2O)_x(OH^-)_y{}^{(4-y)+}$ so leading to very fine precursors for the final oxide. In aqueous solution, H_2O as a polar molecule tends to take protons away from coordinated hydroxide and the reaction equation can be expressed by eqn. (1).[2]

$$Ce(H_2O)_x(OH^-)_y{}^{(4-y)+} + H_2O \rightarrow CeO_2{\cdot}nH_2O + H_3O^+ \quad (1)$$

Compared with conventional heating methods, microwave heating presents a more rapid and simultaneous nucleation due

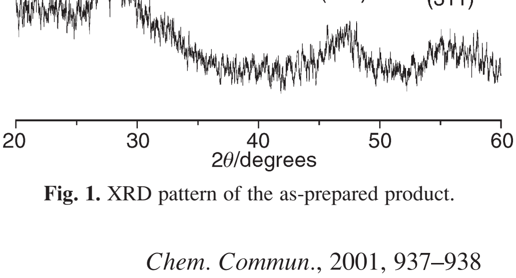

Fig. 1. XRD pattern of the as-prepared product.

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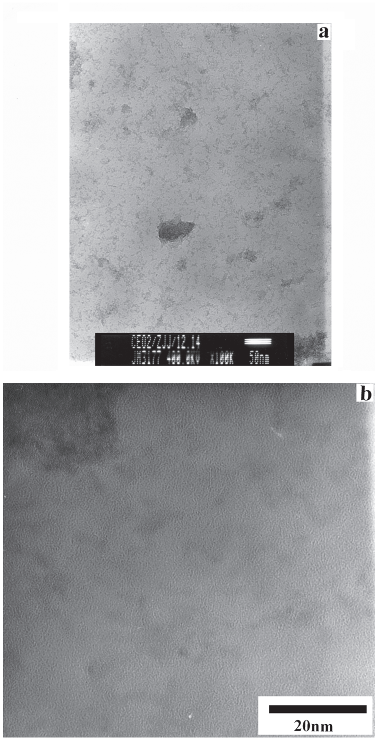

Fig. 2. TEM (a) and HRTEM (b) images of the as-prepared product.

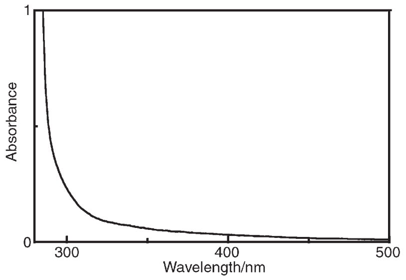

Fig. 3. UV–VIS absorbance spectrum of a toluene suspension containing 0.1046 g L^{-1} of the as-prepared product.

to the fast and homogeneous heating effects of microwaves. Moreover, uniform small particles can be synthesized due to the simultaneous nucleation and homogeneous heating. In addition, PEG, as a dispersion stabilizer, can inhibit segregation so as to obtain homogeneous precipitation. Use of PEG is a general method to synthesize nanocrystalline oxides with some nanocrystalline oxides such as TiO_2 and SnO_2 being successfully prepared *via* this route.

In conclusion, a microwave heating hydrolysis method has been successfully used for the preparation of ultrafine nanocrystalline CeO_2 powders. The advantage of this process is that it is fast, simple and energy efficient. It is predicted that upscaling of the process may lead to large quantities of nanosized CeO_2 crystallites. It also represents a general method to obtain other oxide nanocrystals.

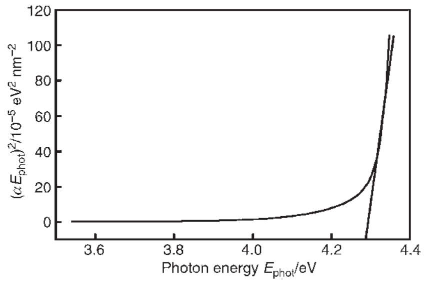

Fig. 4. Plot of $(\alpha E_{phot})^2$ *vs.* E_{phot} for direct transitions, where α is the absorption coefficient and E_{phot} the photon energy. The band gap E_g is obtained by extrapolation to $\alpha = 0$. The data are replotted from Fig. 3.

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Notes and references

‡ A 650 W microwave oven (Sanle General Electric Corp. Nanjing, China) was used for the refluxing system. Powder X-ray diffraction (XRD) patterns were recorded on Shimadzu XD-3A X-ray diffractometer (Cu-Kα radiation, λ= 0.15418 nm). HRTEM images of the products were obtained with a JEOL-4000EX high-resolution transmission electron microscope (HRTEM) with a 400 kV accelerating voltage. UV–VIS absorption spectra were recorded on a Shimadzu UV-Visible 3100 spectrophotometer.

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