Wet Chemical Preparation of Well-dispersed Colloidal Cerium Oxide Nanocrystals

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(Received February 27, 2007; CL-070215)

In this study, a simple one-step wet chemical method was presented to prepare colloidal cerium oxide, CeO_2, nanocrystals. By a direct decomposition of cerium(IV) ammonium nitrate in a solution of 1-octadecene and oleylamine at 180 °C, well-dispersed CeO_2 nanoparticle colloid, with an average size of about 4.5 nm, was obtained.

Nanomaterials have generated a lot of interest because of their unique physical and chemical properties that are significantly different from those of bulk materials. Reducing the particle size to a few nanometers can change the fundamental properties of a material.[1–3] Synthesis and processing of nanocrystalline CeO_2 have drawn considerable attention owing to its wide variety of applications including catalysts for three-way automobile exhaust systems,[4,5] oxygen storage capacity,[6] fuel cells,[7] luminescent materials for violet/blue fluorescence,[8] and the adsorption and reaction of formaldehyde.[9]

To date, many physical and chemical methods have been proposed for the production of crystalline cerium oxide nanoparticles, such as room-temperature solution precipitation, sonochemical synthesis, microemulsion, hydrothermal crystallization, mechanochemical processing, spray pyrolysis, sol–gel method, thermal hydrolysis, solvothermal synthesis, and so on.[10–22] These techniques rely mainly on high pressure, or salt–solvent-mediated high temperature, and the sizes of ceria particles are relatively large. Therefore, to seek a simple approach for low-cost, lower-temperature growth of well-dispersed cerium oxide nanocrystals at atmospheric pressure is essential.

Herein, a simple, low-cost one-step wet chemical method was presented to prepare CeO_2 nanocrystals with small size around 4.5 nm. By direct decomposition of cerium(IV) ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$) and using oleylamine as capping molecule, well-dispersed CeO_2 nanocrystals were prepared. Typically, 0.55 g of (1 mmol) $(NH_4)_2Ce(NO_3)_6$ was added into a mixed solution of 1-octadecene and oleylamine with volume ratio of 2:1 (40 to 20 mL, here) under magnetic stirring. After $(NH_4)_2Ce(NO_3)_6$ was dissolved completely, the reaction temperature was rised to 180 °C rapidly, $(NH_4)_2Ce(NO_3)_6$ was decomposed and the solution became purple owing to the formation of CeO_2 particles. The reaction continued for 2 h. The product was purified and collected by precipitation with ethanol and centrifuging. The final purified sample was dispersed in chloroform. In this experiment, $(NH_4)_2Ce(NO_3)_6$ was obtained from Alfa Aesar, other reagents were purchased from Wako Pure Chemical Industries, Ltd. All the chemicals were reagent grade and used without further purification.

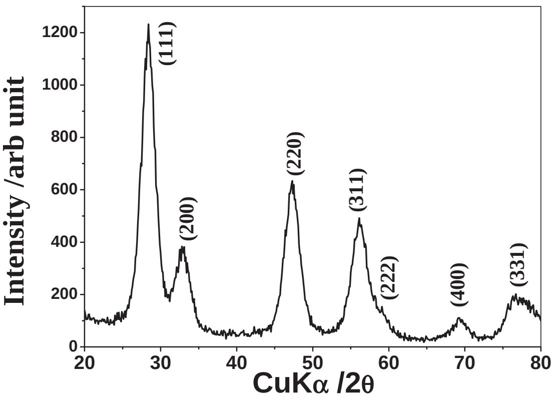

Figure 1. XRD pattern of as-prepared CeO_2 nanoparticles.

The X-ray diffraction (XRD) pattern was taken on a Philips PW1820 diffractometer using Cu Kα radiation at 30 kV and 20 mA. A UV–vis spectrophotometer (UV-1600; Shimadzu Corp.) and a spectrofluorometer (FP-6600; Jasco Inc.) were used to determine the absorption spectra and photoluminescence (PL) emission spectra, respectively. Before emission measurement, the sample suspension was bubbled with ultra-high purity Ar gas for several minutes. The morphologies and microstructures of CeO_2 nanoparticles were examined by a Hitachi S5200 scanning transmission electron microscope (STEM) operating at 30 kV and a JEM-4000EX high-resolution transmission electron microscope (HRTEM) at 400 kV, respectively.

The typical XRD pattern from as-prepared CeO_2 nanoparticles was shown in Figure 1. The diffraction peaks observed show a good match with the JCPDS file of bulk CeO_2 (JCPDS 431002C). There was a considerable broadening of the peaks, suggesting that these nanocrystals were very small in dimension. Using the Scherrer formula, from (111) diffraction, the average size of the nanocrystals was estimated to be around 4.7 nm.

Figure 2 presented the morphologies and microstructures of as-prepared CeO_2 nanocrystals. Viewed at lower magnigications shown in Figure 2a, the nanocrystal shape appeared to be spherical. The average size was estimated to be about 4.5 nm with a narrow size distribution, which was consistent with the estimate obtained from XRD. Also, from the STEM images, it could be seen that the as-prepared nanocrystals are well dispersed and there are no obvious aggregation, which can be further demonstrated from the high-magnification image shown in Figure 2b. From the HRTEM image, it was found that a majority of nanocrystals have well-defined polyhedral shape, showing similar trends in the CeO_2 nanopaticle shape. Usually, for ceria nanoparticles in the size range of 3–10 nm, the particle shape is dominated by a truncated octahedron that is enclosed by

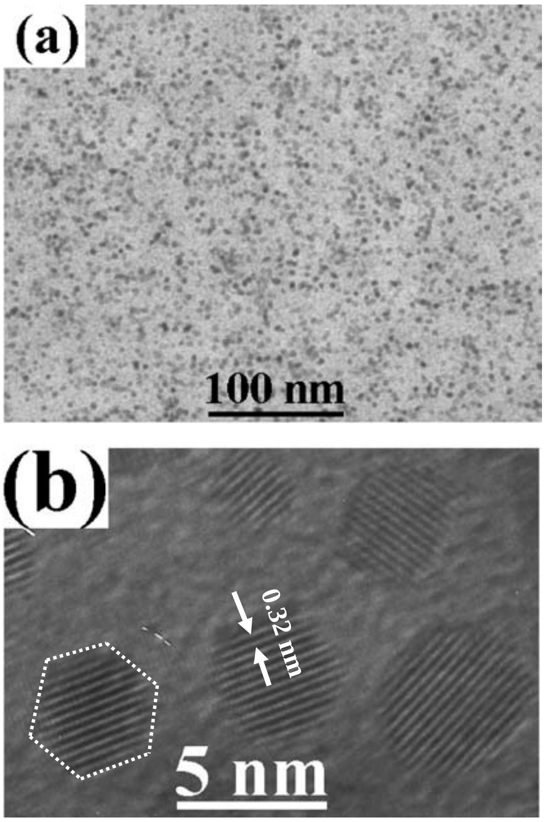

Figure 2. a) STEM and b) HRTEM images of as-prepared CeO_2 nanocrystals.

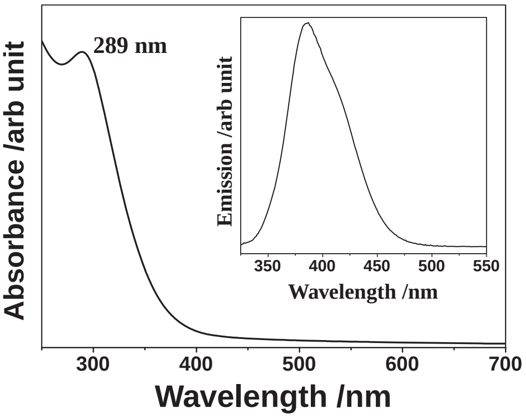

Figure 3. UV–vis absorption and PL emission (inserted, $\lambda_{ex} = 300$ nm) spectra of CeO_2 nanoparticles prepared at 180 °C for 2 h.

the {100} and {111} facets.[11,13] Furthermore, in Figure 2b, the interplanar spacing of (111) facet was about 0.32 nm, which can also be the identification for the ceria nanocrystals.[23]

Figure 3 showed the corresponding UV–vis absorption and room-temperature photoluminescence emission spectra of as-prepared CeO_2 nanoprticles dispersed in chloroform. The measurements were made by using pure chloroform as a blank. As shown in Figure 3, the ceria nanoparticles show a strong absorption below 400 nm with a well-defined absorbance peak at around 290 nm, which is consistent with those reported in the literatures.[24,25] Furthermore, a very obvious emission can be observed at 390 nm for CeO_2 nanoparticles as shown in the inserted PL spectrum in Figure 3.

In summary, a simple, low-cost one-step wet chemical method was developed to prepare well-dispersed CeO_2 nanocrystals. By a direct decomposition of $(NH_4)_2Ce(NO_3)_6$ in 1-octadecene and oleylamine mixture solution, well-dispersed cerium oxide nanoparticles with narrow size distribution were obtained. XRD and TEM images demonstrated that the average size of particles was about 4.5 nm and that most of the particles had a well-defined polyhedral shape. A strong UV–vis absorption and a room-temperature PL emission were also observed at around 289 and 390 nm, respectively.

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