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CeO_2 nanocrystals: Seed-mediated synthesis and size control

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Abstract

This work reports on seed-mediated synthesis and size control of monodispersed CeO_2 nanoparticles. CeO_2 nanoparticles of mean size smaller than 2 nm were first prepared by a simple mixing of aqueous solution of cerium (IV) sulfate and ammonia solution at ambient conditions. Using these as-prepared fine particles as the tiny seeds, tunable sizes of CeO_2 nanoparticles were achieved via a facile hydrothermal treatment. All samples were characterized by X-ray diffraction (XRD), infrared (IR) spectroscopy, UV–vis spectroscopy, and thermogravimetric analysis (TGA). It is shown that in comparison with other inorganic cerium salts such as cerium (III) nitrates, cerium (IV) sulfate appears more suitable for forming CeO_2 nanoparticles at room temperature. Sulfate groups are strongly thermodynamically adsorbed on CeO_2 nanoparticle surfaces. The formation mechanism, surface hydration and sulfation characteristics of the resulting CeO_2 nanoparticles are also discussed.
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1. Introduction

CeO_2 is one of the most important rare-earth oxides that have been widely investigated due to the unique properties and multiple applications such as acting as the three-way catalysts in vehicle emission-control systems [1–3], electrolyte materials of solid oxide fuel cells [4], and ultraviolet blocking materials [5]. Most of the advanced performances of CeO_2 generally appear at small size in particular less than 10 nm, since in that regime the distinct properties are strongly size-dependent and would show significant quantum size effects. Therefore, the priority in tailoring electronic structures for performance improvements is to find the methodologies that can be convenient in getting monodispersed CeO_2 nanoparticles with tunable sizes. Many preparation routes such as hydrothermal synthesis [6], coprecipitation [7], decomposition of oxalate precursors [8], sol–gel [9] and microemulsion methods [3] have been developed for CeO_2 nanoparticles and their solid solutions that are substituted with other metals. However, all these routes met challenges of size control of CeO_2 nanoparticles in the regime below 10 nm. This is probably due to the lack of the knowledge about the formation of tiny ceria seeds that are small enough for activation of grain growth.

In this work, we explored the room-temperature preparation of homogeneous CeO_2 nanoparticles of average size smaller than 2 nm by a simple mixing of cerium sulfate and ammonia solution. Since our recent experimental results

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have shown the advantages of hydrothermal reactions in grain growth of the nanoscale oxides [10], in the present work, we also took the hydrothermal technique to study the size control of CeO_2 nanoparticles by varying the reaction temperatures. Finally, we examined the formation mechanism, the surface chemistry, and the absorption properties.

2. Experimental

All chemical reagents used in this work are analytic grade from Sinopharm Medicine Company, China. $Ce(SO_4)_2{\cdot}4H_2O$ was dissolved in distilled water and formed a clear solution with a concentration of 0.4 M (for a parallel experiment, $Ce(NO_3)_3{\cdot}6H_2O$ is also used). To this solution, ammonia solution was added drop-wise at room temperature with continuous stirring. A yellow suspension appeared and gradually became brown in color with continuous addition of the ammonium solution. The final volume ratio of ammonia solution and cerium sulfate or nitrate solution is 1:5. The resulting room-temperature precipitates were filtered and washed with distilled water for several times and dried at 80 °C in air. These samples thus obtained were named as RT-S and RT-N, where S and N denote the samples using cerium sulfate and nitrate as the starting materials.

Size control of CeO_2 nanoparticles was achieved by a hydrothermal treatment on the tiny seeds RT-S using a procedure as follow: the tiny seeds prepared at room-temperature were transferred into Teflon-lined stainless steel autoclaves which were allowed to react at 120, 140, 160, 180, 200, 220 °C for 5 h, respectively. When the formation reactions were completed, the autoclaves were cooled naturally to room temperature. Samples obtained after being filtered and dried were named as RT-S1205, RT-S1405, and so on.

X-ray powder diffraction patterns of CeO_2 nanoparticles were recorded on a D/max-2500 diffractometer (copper target, RIGAKU, Japan). High-purity nickel (99.9%, Shanghai Chemical Reagents Co.) was used as the internal standard. The mean crystallite size (D) of sample was calculated from the most intense XRD peak (1 1 1) in accordance with the Scherrer formula: $D = 0.9\lambda/\beta \cos\theta$, where λ is the X-ray wavelength used, θ and β are the diffraction angle and full-width at half-maximum of the (1 1 1) peak, respectively. Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrometer in the 400–4000 cm^{-1} range at a resolution of 4 cm^{-1}. The samples were ground carefully and were then pressed into pellets with KBr powders (analytical grade, $\geq$99%) at a weight ratio of 1:100 for CeO_2:KBr.

Thermal behaviors of CeO_2 nanoparticles were examined using a Netzsch STA449C thermogravimetric analyser at a heating rate of 15 °C/min in nitrogen atmosphere from room temperature to 1000 °C. All samples were first dried for 12 h at 80 °C before measurements. The optical diffuse reflectance spectra of CeO_2 nanocrystals were obtained using Lambda 900 UV–vis Spectrometer at room temperature in a wavelength region between 200 and 1000 nm. $BaSO_4$ was used as a reference material. The reflectance spectra were converted to the Kubelka–Munk remission function defined by $F(R) = (1 - R)^2/2R$, where R is the reflectance.

3. Results and discussion

3.1. Effects of starting cerium salts on formation reactions at room temperature

Fig. 1 shows the XRD pattern of sample RT-S derived using cerium sulfate as the starting material. The standard data for fcc CeO_2 (JCPDS No. 43-1002) are given as the vertical bars at the bottom of Fig. 1. The XRD data for sample RT-N prepared using cerium nitrate salts as the starting material are also shown for comparison. It is clear that all Bragg reflections for samples RT-S and RT-N agree well with those of standard CeO_2, which indicates the formation of pure-phase CeO_2 in a cubic fluorite structure. All reflections in Fig. 1 are also noticeably broadened, showing the fine nature of these CeO_2 particles. The mean crystallite size of RT-S calculated from the most intense XRD peak (1 1 1) using Scherrer formula was smaller than 2 nm, compared with that of approximately 12 nm for RT-N. Therefore, cerium sulfate is proved to be advantageous over cerium nitrate in getting very small sizes of CeO_2.

There are two primary factors that directly determine the crystalline size of samples, namely, nucleation and crystal growth process [11,12]. In case of nucleation from cerium (III) nitrate, the formation reaction at room temperature may require an oxidation process from Ce^{3+} to Ce^{4+}. This process could be most likely to occur by addition of given concentration of ammonia solution since basic solution favors Ce^{4+} compared with Ce^{3+}. Therefore, the rate and the number of nucleation of hydroxide from cerium (III) nitrate may be slower and fewer than those from cerium (IV) salts. Reversibly, the starting precipitate from cerium (IV) salt may form plenty of nucleation centers of hydrated

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