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Shape-selective synthesis of CeO_2 via an EDTA-assisted route

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Abstract Nanoparticles and sub-microrods of cubic CeO_2 were selectively prepared via an ethylendiamine tetraacetate (EDTA)-assisted route. They were characterized by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and infrared (IR) techniques. Controlling the reaction process, we obtained CeO_2 with different shapes. Sub-microrods were formed via an incomplete reaction while uniform nanoparticles were formed through a complete reaction between $NaClO_3$ and Ce–EDTA complexes. The addition of EDTA was critical to obtain CeO_2 sub-microrods and nanoparticles. Other experimental conditions, such as EDTA/Ce^{3+} molar ratio and the reaction time were of importance in the final product morphology. A possible formation mechanism of CeO_2 was discussed.

Introduction

Shape-selective synthesis of inorganic nanomaterials is of scientific and technological importance due to their unique shape-dependent properties and their promising application. Therefore, great efforts have been devoted to the synthesis of inorganic particles with various morphologies [1, 2]. Cerium (IV) oxide (CeO_2) with a cubic fluorite-type structure, is an important material because its application is not only as an oxygen ion conductor in solid oxide fuel cells and oxygen monitors, but also as abrasive materials for chemical–mechnical planarization of advanced integrated circuits [3, 4]. Several techniques that include hydrothermal synthesis [5, 6], coprecipitation [7], flux method [8] and mechanical mixing [9] have been developed for the production of ceria. However, the reports on CeO_2 of different shapes selectively synthesized are scarce [5]. In particular, using the incomplete/complete reaction to control the shape is rarely reported [5–9].

M-EDTA is one of suitable precursors for the preparation of various materials under hydrothermal conditions. In addition, EDTA chelate precursors have been useful for controlling the crystal morphology under hydrothermal aging [10, 11].

In this paper, an EDTA-assisted method has been developed to selectively synthesize CeO_2 sub-microrods and nanoparticles, using $Ce(NO_3)_3$ and $NaClO_3$ aqueous solutions as the reactants and EDTA as the modification agent. Furthermore, the shape-selective synthetic mechanism was investigated.

Experimental section

All chemicals ($Ce(NO_3)_3 \cdot 6H_2O$, $Na_2H_2EDTA \cdot 2H_2O$ and $NaClO_3$) were reagent grade and used without further purification. In a typical experiment, 0.217 g $Ce(NO_3)_3 \cdot 6H_2O$ was put into 5 mL of deionized water under stirring to form a homogeneous solution. Subsequently,

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5 mL of 0.1 mol/L $Na_2H_2EDTA \cdot 2H_2O$ aqueous solution was introduced into the above homogeneous solution under continuous stirring. After a few minutes, 2.5 mL of 0.5 mol/L $NaClO_3$ aqueous solution was added into the above solution drop by drop under vigorous stirring. Then 12 mL slurry was transferred into a Teflon-lined stainless steel autoclave, sealed, and maintained at 180 °C for 8 h (sample 1) or 24 h (sample 2). After that, the autoclave was cooled down to room temperature naturally. The supernatant liquid was discarded and the remaining product was washed with deionized water and ethanol in sequence several times, and then separated by centrifugation. The product was dried in a vacuum oven at 60 °C for 12 h and then sample 1 was calcined with a muffle oven at 350 °C in air for 4 h (sample 3).

The samples were characterized by XRD on a Japan Rigaku D/Max-γA 200 X-ray diffractometer with CuKα radiation (λ = 1.541 78 Å). TEM was carried out on a JEM-100CXII at an accelerating voltage of 100 kV. The samples for these measurements were dispersed in absolute ethanol by vibration in the ultrasonic pool. Then, the solutions were dropped onto a copper grid coated with amorphous carbon films and dried in air before measurement. Infrared spectra of the samples were obtained on a Nicolet T-IR5DX spectrometer.

Results and discussion

The phase purity of the product was examined by the XRD pattern. Figure 1 shows the XRD patterns of the sub-microrods (sample 3) and nanoparticles (sample 2). All the peaks can be indexed to a face-centred cubic pure phase (space group: *Fm*3*m* (225)) of ceria (JCPDS no. 81–0792). The morphology of the obtained product was shown in the TEM images (Fig. 2). The length of the sub-microrods was about 12 μm and the diameter was about 250 nm. The size of the crystalline nanoparticles was about 40 nm, and all the resulting particles grew and developed into a good crystalline structure with polyhedral shape.

To understand the formation mechanism, the detailed growth process of CeO_2 was carefully followed by time-dependent experiments. The effect of reaction time was investigated by fixing the temperature at 180 °C for 2, 6, 8, 12, 24 h, respectively. After heating for 2 h, the morphology of the product was microsheets as shown in the TEM images (Fig. 3a), but the product had poor crystallinity (inset in Fig. 3a). These microsheets should be a complex from the strong coordination interaction between cerium ions and EDTA. We believed that, before the hydrothermal reaction, the coordination occurred between EDTA and Ce^{3+} and formed complex, which was demonstrated by a change of the pH value. After EDTA solution

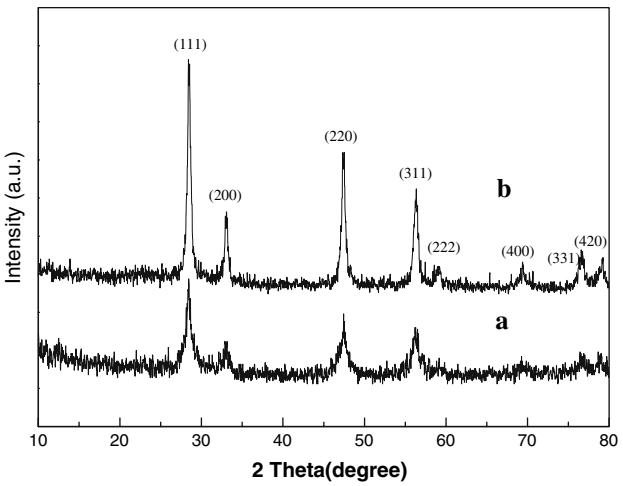


Fig. 1 XRD patterns of the as-obtained samples: (**a**) sub-microrods and (**b**) nanoparticles

(pH ≈ 5) was added dropwise to $Ce(NO_3)_3$ aqueous solution (pH ≈ 4.5) with stirring, the pH value of the resulting mixture was about 1.5. This phenomenon was attributed to the coordination reaction between EDTA and Ce^{3+}. In order to further investigate whether there was a coordination interaction between EDTA and cerium ions after hydrothermal 2 h, the FT-IR spectra were recorded as shown in Fig. 4. For well comparison, we also showed the IR spectra for H_4EDTA. The vibration frequencies of interest were the characteristic frequencies of the carboxyl group and the C–N anti-symmetrical and symmetrical stretching. The strongest and most characteristic absorption band for the carboxylate group (COO^-) was in the 1,570–1,660 cm^{-1} region and was due to the anti-symmetrical vibration of the COO^- group [12, 13]. The peak due to anti-symmtrical stretching vibration of COO^- group for Ce-EDTA occurred at the characteristic range 1596.65 (1,615–1,590 cm^{-1}) [12, 13] for metal–carboxyl bonding. It has been noted that the symmetrical and antisymmetrical C–N stretching bands in the Fig. 4b shift to longer wavelengths (smaller frequencies) compared with H_4EDTA (Fig. 4a). These results suggested that the cerium-nitrogen interaction occurred [14].

The evolution process of sub-microrods and nanoparticles from the microsheets at 180 °C was presented in Fig. 3. After 2 h, The XRD pattern of the microsheets indicated that CeO_2 had not been produced but Ce–EDTA complexes appeared (See ESM, Fig. 1). When the hydrothermal reaction time was extended to 6 h, a mixture of the sheet-like particles and sub-microrods could be clearly observed from the TEM as shown in Fig. 3b. When the time was prolonged to 8 h, most sheet-like particles disappeared and sub-microrods with 250 nm in diameter and 12 μm in length were formed (Fig. 3c). The diffraction of CeO_2 was obviously strengthened by the XRD (See ESM,

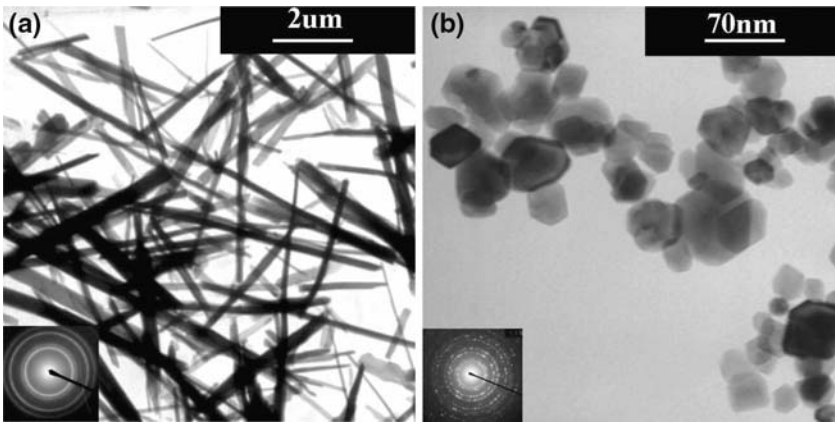


Fig. 2 TEM images of samples: (**a**) sub-microrods and (**b**) nanoparticles

Fig. 1). In contrast, when the reaction time was prolonged to 12 h, rods consisting of nanoparticles were the predominant product (Fig. 3d). Furthermore, the sub-microrods had a tendency to break. After 24 h, the sub-microrods disappeared completely, and nanoparticles appeared (Fig. 2b). If the reaction time was fixed at 8 h, then the product was calcined with a muffle oven at 350 °C in air for 4 h with heating carefully, TEM images revealed that the sub-microrod shape of CeO_2 sustained after thermal treatment. The crystalline nature of the resultant CeO_2 sub-microrods and nanoparticles was verified by the selected area electron diffraction (SAED) patterns (inset in Fig. 2), which were basically annular patterns. Like the XRD profile, the two annular patterns could be indexed to the fluorite crystal structure. It could be seen from the TEM images that the variation in the morphologies of the products with different reaction time was significant. The evolution process was similar to that of the needle-like barium sulfate using a barium-EDTA chelate precursor [15].

The presence of EDTA was crucial for the formation of CeO_2 sub-microrods and nanoparticles. Controlled experi-

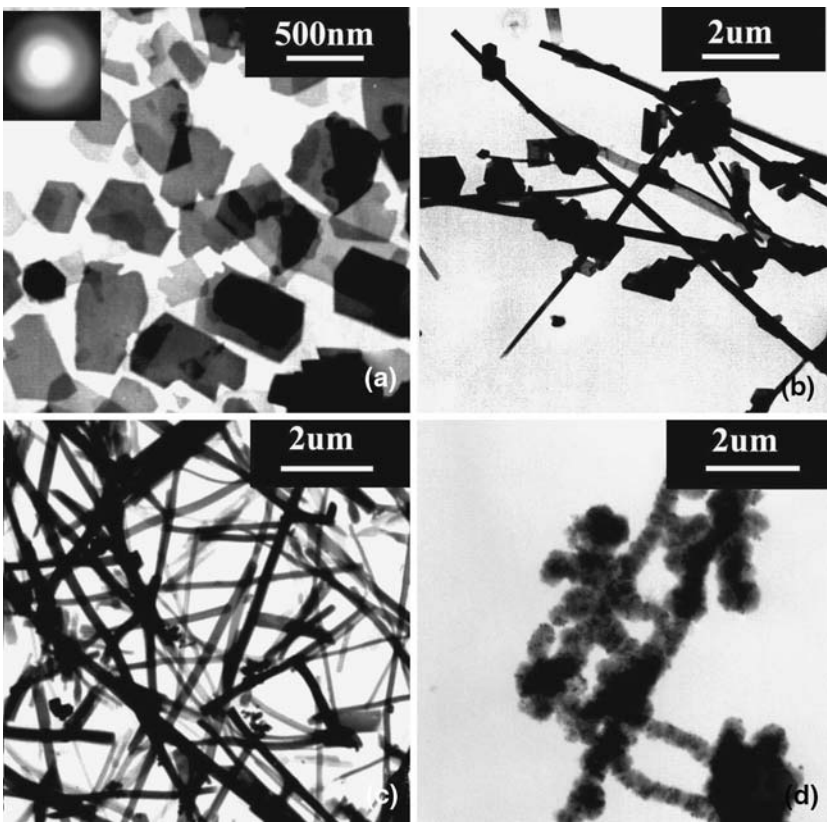


Fig. 3 Time-dependent growth progress illustrated by TEM images under hydrothermal conditions. (**a**) 2 h, (**b**) 6 h, (c) 8 h and (**d**) 12 h

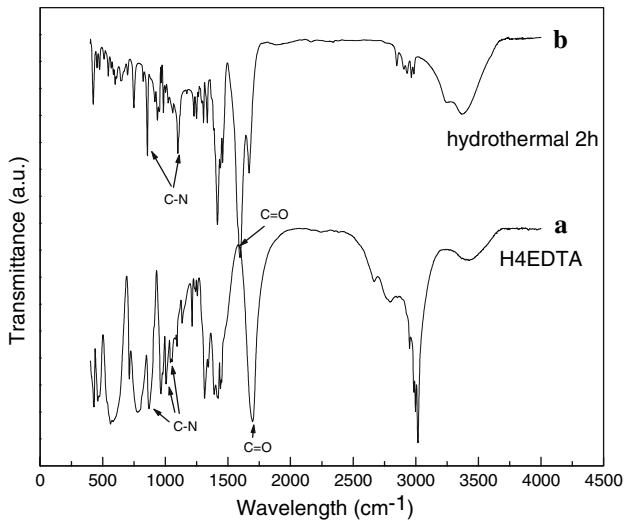


Fig. 4 FT-IR spectra of the H_4EDTA (**a**) and the sample in 180 °C hydrothermal reaction time 2 h (**b**)

ments have shown that only CeO_2 particles (average diameter ca. 2 μm) were obtained without EDTA (See ESM, Fig. 2A), and a sphere-like aggregation with an average width of 200 nm which consisted of many nanoparticles (See ESM, Fig. 2B) were formed at low concentration of EDTA. We concluded that, Ce–EDTA complex was unstable in the small [EDTA]/[Ce^{3+}]molar ratio, thus, Ce^{3+} ions were easily oxidized by the ClO_3^-, which was similar to La–EDTA complexes [16]. In other way, the template effect decrease in the small [EDTA]/[Ce^{3+}] molar ratio, so CeO_2 nanoparticles formed.

In fact, there are lone pair electrons on nitrogen and oxygen atoms in EDTA, which provide the possibility that the EDTA could combine with the Ce^{3+} ions to form Ce–EDTA complexes. The complexes might serve as molecular templates in control of the crystals growth. The stability of the complexes results from the multiple sites within the ligand that gave rise to a cage-like structure, and is expected to decrease with the increase of the temperature. With the stability of the Ce–EDTA complexes decreased, the Ce^{3+} ions dissociated slowly and the ClO_3^- ions oxidized the Ce^{3+} ions to the Ce^{4+} under the acid condition that provided by the reaction between Ce^{3+} and EDTA. As Ce^{4+} ions were easily hydrolyzed, so the CeO_2 formed by the dehydration of $CeO_2 \cdot nH_2O$ which was the hydrolysis result of Ce^{4+}. Meanwhile, the mixture phases Ce–EDTA complexes and CeO_2 coexisted, which was conformed by the XRD analysis (See ESM, Fig. 1). The chemical reactions course can be expressed concisely as follow:

$$Ce^{3+} \xrightarrow{EDTA} Ce\text{–}EDTA \xrightarrow[H^+]{ClO_3^-} Ce^{4+}$$

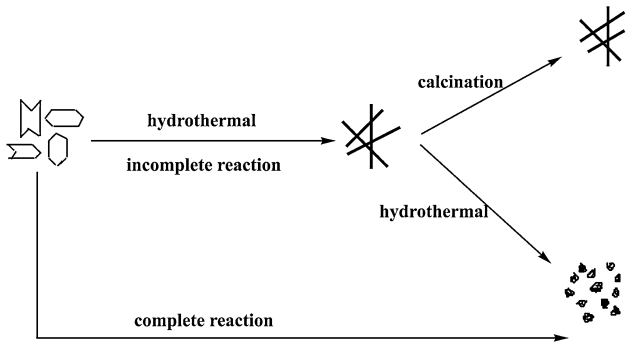
$$\xrightarrow{\text{hydrolysis}} CeO_2 \cdot nH_2O \xrightarrow{\text{dehydration}} CeO_2$$

At appropriate reaction time, the uniform sub-microrods appeared with the mixture phases (Ce–EDTA and CeO_2) (sample 1). It was noticed that this was an incomplete reaction, because excessive $NaClO_3$ would react with Ce–EDTA complexes continuously. When sample 1 calcined, the complexes phase disappeared and the CeO_2 phase remained, more importantly, the rod shape maintained after thermal treatment (sample 3). However, when extending hydrothermal time on the base of sample 1, the Ce–EDTA complexes dissociated unceasingly and the reaction went on, so the CeO_2 phase strengthened at the cost of the decrease of the complexes phase. Eventually, only CeO_2 phase existed.

The formation of sub-microrods and nanoparticles could be depicted as in Scheme 1.

Conclusion

In summary, a simple EDTA-assisted hydrothermal process could be used for the selectively synthesize of CeO_2. Uniform sub-microrods and nanoparticles of cubic CeO_2 were selectively prepared by controlling the reaction process. Sub-microrods were formed by calcination and nanoparticles were formed by continuous reaction between the ClO_3^- and complexes. In the process of the CeO_2 formation, EDTA acts not only cheleating ligand but also template, which is an important role in forming the CeO_2. Meanwhile, the reaction time, reaction temperature and the [Ce^{3+}]/[EDTA] molar ration were all influenced the morphology of CeO_2. This one-pot solution approach offers an example for shape-selective synthesis based on incomplete/complete reaction, which also could be further extended as a facile route to access other inorganic materials with different shapes.



Scheme 1 Schematic illustration of the possible formation process for sub-microrods and nanoparticles of CeO_2

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