

Synthesis and Characterization of Single-Crystal Ce(OH)CO₃ and CeO₂ Triangular Microplates

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Single-crystal cerium hydroxide carbonate (Ce(OH)CO₃) triangular microplates with the hexagonal phase have been successfully synthesized by a hydrothermal method at 150 °C using cerium nitrate (Ce(NO₃)₃·6H₂O) as the cerium source, aqueous carbamide as both an alkaline and carbon source, and cetyltrimethylammonium bromide (CTAB) as a surfactant. Single-crystal ceria (CeO₂) triangular microplates have been fabricated by a thermal decomposition–oxidation process at 650 °C for 7 h using single-crystal Ce(OH)CO₃ microplates as the precursor. The shape of the Ce(OH)CO₃ microplate was sustained after thermal decomposition–oxidation to CeO₂. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM), differential scanning calorimetric analysis (DSC), and thermogravimetric analysis (TG).

Introduction

In the past decade, extensive research has been carried out in the design and preparation of nanostructures with different shapes and sizes because of their corresponding novel properties and potential applications.^{1–3} Recently, various methods have been employed to control the shape and size of nanomaterials. For example, a biological synthetic system involving an extract from the lemongrass plant was adopted for generating a high percentage of thin, flat, single-crystal gold nanotriangles.⁴ Truncated triangular silver nanoplates were obtained through a seed-mediated growth in the presence of micelles of cetyltrimethylammonium bromide (CTAB).⁵ Single-crystal In(OH)₃ nanocubes were formed by an oxidation hydrothermal route, and In₂O₃ nanocubes were subsequently obtained by calcination of In(OH)₃.⁶ Qi et al. reported the synthesis of single-crystal Ce(OH)CO₃ rods by a sonochemical method and CeO₂ rods by the thermal conversion of the as-synthesized Ce(OH)CO₃.⁷

Cerium hydroxide carbonate (Ce(OH)CO₃) has been extensively studied and employed because of its optical properties.^{8–10} Ce(OH)CO₃ has either orthorhombic or hexagonal structure and is composed of Ce³⁺, CO₃²⁻, and hydroxyl ions. Ceria is of interest for widespread applications in catalysts,^{11–13} fuel cells,¹⁴ ultraviolet absorbers,¹⁵ hydrogen storage materials,¹⁶ oxygen sensors,¹⁷ optical devices,¹⁸ polishing materials,¹⁹ etc. It is well-known that the new properties and applications of materials are related to their

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- (1) Service, R. F. *Science* **1996**, *271*, 920–922.
- (2) Sun, Y. G.; Mayers, B.; Xia, Y. N. *Nano. Lett.* **2003**, *3*, 675–679.
- (3) Alivisatos, A. P. *Science* **1996**, *271*, 933–937.
- (4) Shankar, S. S.; Rai, A.; Ankamwar, B.; Singh, A.; Ahmad, A.; Sastry, M. *Nature* **2004**, *3*, 482–488.
- (5) Chen, S. H.; Carroll, D. L. *Nano. Lett.* **2002**, *2*, 1003–1007.
- (6) Tang, Q.; Zhou, W. J.; Zhang, W.; Ou, S.; Jiang, K.; Yu, W. C.; Qian, Y. T. *Cryst. Growth Des.* **2005**, *5*, 147–150.

- (7) Qi, R. J.; Zhu, Y. J.; Cheng, G. F.; Huang, Y. H. *Nanotechnology* **2005**, *16*, 2502–2506.
- (8) Chen, S.; Yu, S. H.; Yu, B.; Ren, L.; Yao, W.; Cölfen, H. *Chem.—Eur. J.* **2004**, *10*, 3050–3058.
- (9) Han, Z. H.; Guo, N.; Tang, K. B.; Yu, S. H.; Zhao, H. Q.; Qian, Y. T. *J. Cryst. Growth* **2000**, *219*, 315–318.
- (10) Li, G.; Feng, S.; Li, L. *J. Solid State Chem.* **1996**, *126*, 74–79.
- (11) Reddy, B. M.; Khan, A.; Yamada, Y.; Kobayashi, T.; Lorient, S.; Volta, J. C. *Langmuir* **2003**, *19*, 3025–3030.
- (12) Bera, P.; Gayen, A.; Hegde, M. S.; Lalla, N. P.; Spadaro, L.; Frusteri, F.; Arena, F. J. *Phys. Chem. B* **2003**, *107*, 25, 6122–6130.
- (13) Asadullah, M.; Fujimoto, K.; Tomishige, K. *Ind. Eng. Chem. Res.* **2001**, *40*, 5894–5900.
- (14) Jacobs, G.; Williams, L.; Graham, U.; Sparks, D.; Davis, B. H. J. *Phys. Chem. B* **2003**, *107*, 10398–10404.
- (15) Li, R. X.; Yabe, S.; Yamashita, M.; Momose, S.; Yoshida, S.; Yin, S.; Sato, T. *Solid State Ionics* **2002**, *151*, 235–241.
- (16) Sohlberg, K.; Pantelides, S. T.; Pennycook, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 6609–6611.
- (17) Jasinski, P.; Suzuki, T.; Anderson, H. U. *Sens. Actuators, B* **2003**, *95*, 73–77.
- (18) Goubin, F.; Rocquefelte, X.; Whangbo, M. H.; Montardi, Y.; Brec, R.; Jobic, S. *Chem. Mater.* **2004**, *16*, 662–669.
- (19) Shchukin, D. G.; Caruso, R. A. *Chem. Mater.* **2004**, *16*, 2287–2292.

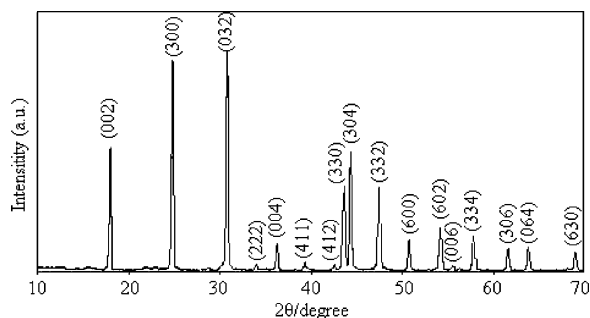


Figure 1. XRD pattern of the as-synthesized $\text{Ce}(\text{OH})\text{CO}_3$ triangular microplates.

shapes and sizes. However, the controllable synthesis of triangular platelike $\text{Ce}(\text{OH})\text{CO}_3$ and CeO_2 structures is still a challenge to material scientists. Herein, we report a simple method for the synthesis of $\text{Ce}(\text{OH})\text{CO}_3$ and CeO_2 triangular microplates with single-crystal structure.

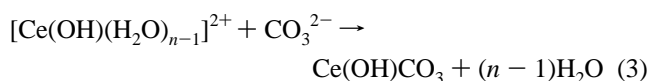
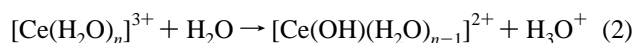
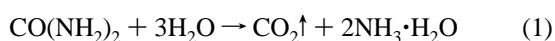
Experimental Section

In a typical synthesis, 0.005 mol of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.01 mol of cetyltrimethylammonium bromide (CTAB) were dissolved in 40 mL of a carbamide solution with a concentration of 0.5 mol/L. The solution was transferred to a Teflon-lined stainless steel autoclave and maintained at 150 °C for 16 h; it was then air-cooled to room temperature. The resulting white precipitate was collected, washed with water, and dried in air at room temperature. The as-synthesized $\text{Ce}(\text{OH})\text{CO}_3$ was calcined to produce straw-yellow CeO_2 in air at 650 °C for 7 h. X-ray powder diffraction (XRD) patterns were recorded using a D/MAX-500 X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$ at 40 kV and 70 mA). SEM images and TEM images were taken with a JSM-6700F field-emission scanning electron microscope and a JEM-2000EX transmission electron microscope, respectively. Differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TG) were carried out with a Netzsch-449c simultaneous TG-DTA/DSC apparatus (Germany) with a heating rate of 10 °C min^{-1} under flowing air.

Results and Discussion

Figure 1 shows a typical XRD pattern of the as-synthesized $\text{Ce}(\text{OH})\text{CO}_3$ triangular microplates by hydrothermally treating a solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, CTAB, carbamide, and deionized water at 150 °C for 16 h. All peaks in this pattern can be well-indexed to a pure hexagonal phase of $\text{Ce}(\text{OH})\text{CO}_3$ (space group: $P\bar{6}2c$) with calculated lattice constants $a = 12.52 \text{ \AA}$ and $c = 10.00 \text{ \AA}$, which is in good agreement with the JCPDS file for $\text{Ce}(\text{OH})\text{CO}_3$ (JCPDS 52-0352). No impurity peaks are observed, indicating a high purity of the final products.

The reaction process for the formation of $\text{Ce}(\text{OH})\text{CO}_3$ may be summarized by the following reactions



Typical SEM and TEM images of $\text{Ce}(\text{OH})\text{CO}_3$ triangular

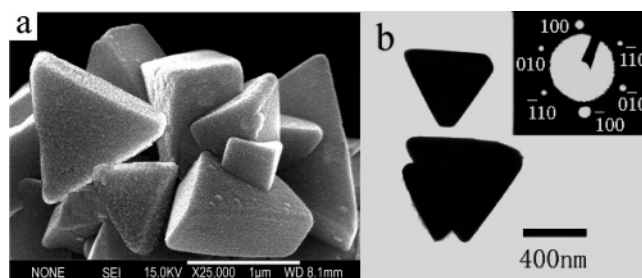


Figure 2. (a) SEM and (b) TEM images of $\text{Ce}(\text{OH})\text{CO}_3$ triangular microplates.

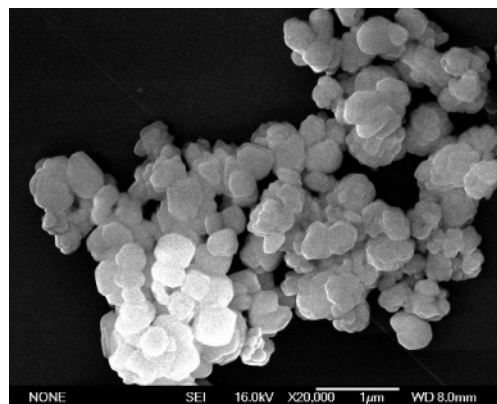


Figure 3. SEM image of $\text{Ce}(\text{OH})\text{CO}_3$ particles prepared in the absence of CTAB.

microplates are shown in panels a and b, respectively, of Figure 2. SEM observation (Figure 2a) reveals that the as-synthesized $\text{Ce}(\text{OH})\text{CO}_3$ possesses regular triangular platelike structures with sharp corners and a smooth surface. The edge lengths range from 400 nm to 1.2 μm and the thickness is about 300–500 nm. The triangular microplates of as-synthesized products are further confirmed by the TEM image (Figure 2b). The edge lengths are consistent with those of the SEM image (Figure 2a). The electron-diffraction (ED) pattern (Figure 2b inset) taken from a triangular microplate can be assigned to hexagonal $\text{Ce}(\text{OH})\text{CO}_3$, indicating that each triangle is a single crystal with its [001] orientation parallel to the electron beam.

In the hydrothermal process, carbamide was hydrolyzed into CO_2 and $\text{NH}_3 \cdot \text{H}_2\text{O}$. The cerium ions can exist in the form of $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ in aqueous solution, and then $[\text{Ce}(\text{H}_2\text{O})_n]^{3+}$ is changed into $[\text{Ce}(\text{OH})(\text{H}_2\text{O})_{n-1}]^{2+}$; finally, $\text{Ce}(\text{OH})\text{CO}_3$ is obtained by the reaction between $[\text{Ce}(\text{OH})(\text{H}_2\text{O})_{n-1}]^{2+}$ and CO_3^{2-} . The surfactant CTAB plays an important role in the formation of $\text{Ce}(\text{OH})\text{CO}_3$ triangular microplates. When the reaction was carried out without the aid of CTAB, only spherical particles were observed (Figure 3). It is supposed that the triangular microplate is obtained through a seed-mediated growth in the presence of micelles of cetyltrimethylammonium bromide (CTAB). CTAB, as a capping reagent, is adsorbed selectively on the different planes of $\text{Ce}(\text{OH})\text{CO}_3$ seeds, helps to lower the surface tension and stabilize the plates, and results in a different growth rate of different planes to form the triangular platelike structures. The real formation mechanism of triangular $\text{Ce}(\text{OH})\text{CO}_3$ structures needs further investigation.

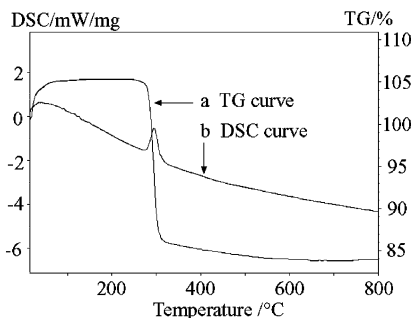


Figure 4. DSC–TG pattern of the as-synthesized Ce(OH)CO₃ triangular microplates under flowing air.

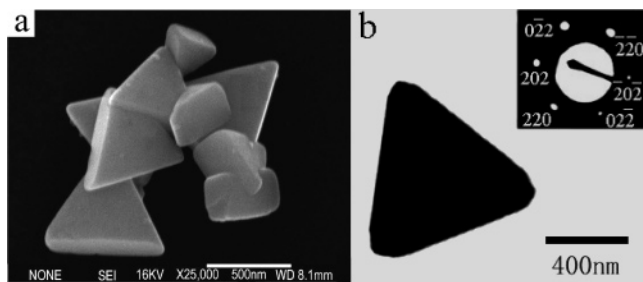


Figure 5. (a) SEM and (b) TEM images of CeO₂ triangular microplates by calcining Ce(OH)CO₃ triangular microplates in air at 650 °C for 7 h.

Figure 4 is a typical DSC–TG pattern of the as-synthesized Ce(OH)CO₃ triangular microplates. The TG curve (Figure 4, curve a) shows that Ce(OH)CO₃ starts to decompose (weight loss) at about 290 °C. The total weight loss between 290 and 600 °C is measured to be about 21.86%; this value is close to the result in the theoretical value calculated from the following reaction



The DSC curve (Figure 4, curve b) shows one endothermic peak with a maximum located at 294.4 °C. The temperature range of the endothermic peak in the DSC curve fits well with that of weight loss in the TG curve, corresponding to endothermic behavior during the thermal decomposition–oxidation of Ce(OH)CO₃ to CeO₂.

After Ce(OH)CO₃ triangular microplates are calcined in air at 650 °C for 7 h, CeO₂ triangular microplates are formed. As shown in Figure 5, SEM and TEM images reveal that the microplate shape of Ce(OH)CO₃ was sustained after thermal decomposition–oxidation to CeO₂. The edge lengths and thickness of CeO₂ triangular microplates are in the range of 300 nm–1 μm and 100–200 nm, respectively. In comparison with Ce(OH)CO₃ in Figure 2, the sizes of CeO₂ triangular microplates are smaller than that of Ce(OH)CO₃ because the density of the former is higher than that of the latter. The ED pattern (Figure 5b inset) recorded on an

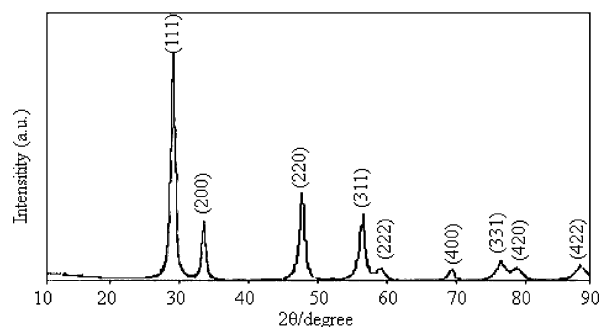


Figure 6. XRD patterns of the obtained CeO₂ triangular microplates.

individual CeO₂ triangular microplate indicates that each triangle is a single crystal with its [111] orientation parallel to the electron beam.

Figure 6 shows the XRD pattern of CeO₂ triangular microplates obtained by calcination of the as-synthesized Ce(OH)CO₃. All of the peaks can be well-indexed to a pure face-centered cubic (fcc) structure of CeO₂ (space group: *Fm* $\bar{3}$ *m*) with lattice constant $a = 5.412 \text{ \AA}$, which is in good agreement with the JCPDS file for CeO₂ (JCPDS 81-0792). It is worth noting that the overwhelmingly intensive diffraction peak is located at $2\theta = 28.660^\circ$, which is from the [111] lattice plane of fcc CeO₂. This clearly demonstrates that the basal plane, i.e., the top crystal plane of the microplates, should be the [111]. It is known that this structural feature is quite common for the nanoplates, because similar structure were also found in the cases of silver,²⁰ gold,⁴ and CdS²¹ plates. It is highly possible that this plane may possess the lowest surface tensions, as in the case of the [111] plane of lead crystal.²²

Conclusion

In summary, we have demonstrated a simple route for preparing single-crystal Ce(OH)CO₃ triangular microplates in the presence of the surfactant CTAB by hydrothermal treatment. Furthermore, CeO₂ triangular microplates with single-crystal structures are obtained after the calcination of the Ce(OH)CO₃ precursor. Surfactant CTAB plays an important role in the growth of uniform Ce(OH)CO₃ triangular microplates, and the triangular shape of single-crystal Ce(OH)CO₃ was sustained in the conversion process to CeO₂. It is expected that these materials with triangular structures can find potential applications in multiple fields as catalysts, storage hydrogen devices, and optically or electrically functional host materials.

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(20) Jin, R.; Cao, Y. W.; Mirkin, C. A.; Kelly, K. L.; Schata, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901–1903.

(21) Pinna, N.; Weiss, K.; Sack-Kongehl, H.; Vogel, W.; Urban, J.; Pileni, M. P. *Langmuir* **2001**, *17*, 7982–7987.

(22) Heyraud, J.; Metois, C.; *J. J. Surf. Sci.* **1983**, *128*, 334–342.