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LETTER

Facile synthesis of ceria rhombic microplates

Dengsong Zhang · Lei Huang · Jianping Zhang · Liyi Shi

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Introduction

Interest in the fabrication of inorganic particles with controlled size and shape is driven by their potential unique and tunable physical properties and the desire to engineer advanced bulk materials from micro- or nano-scale building blocks [1, 2]. CeO_2 is a technologically important rare earth material because of its wide applications as fast ion conductors, oxygen storage capacitors, catalysts, UV blockers, polishing materials, and optical displays [3–7]. Both single crystal and polycrystalline ceria micro- or nano-structures with different shapes, such as nanopolyhedra [8], nanocubes [9], nanospheres [10], nanorods/nanowires [11–16], core-shell nanowires [17], nanotubes [18, 19], and triangular microplates [20] have been synthesized by us and other research groups in recent years. It is found that the properties and applications of micro- or nano-materials are related to their morphologies and sizes. For example, Guo et al. [20] synthesized CeO_2 triangular microplates by a thermal decomposition–oxidation process using $Ce(OH)CO_3$ microplates as the precursor, and suggested that these materials with triangular structures could find potential applications in multiple fields as catalysts, storage hydrogen devices, and optically or electrically functional host materials. Zhong et al. [21] reported that the flowerlike micro-ceria can be used as not only an effective sorbent for the removal of pollutants in water treatment but also as an excellent support for gold nanoparticles to remove CO by catalytic oxidation, demonstrating a promising potential in environmental remediation. Sun et al. [22] reported that the monodisperse flowerlike ceria microspheres can be used as a support for catalysts with various purposes. Previous reports show that micro-ceria with the special morphology has a potential application in various fields. However, few studies have been reported on the fabrication of CeO_2 rhombic microplates.

Recently, we synthesized CeO_2 nanoplates, nanorods, and nanotubes using CTAB as a surfactant under a low-temperature hydrothermal condition [23], and we also developed a facile template-free liquid precipitation method to synthesize CeO_2 nanorods, nanotubes, nanowires, and nanocubes [24]. Herein, we first report a simple surfactant-assisted method to synthesize CeO_2 rhombic microplates.

Experimental section

All chemicals supplied by Shanghai Chemical Reagent Company (P. R. China) were of analytical grade, and were used as purchased without further purification. Deionized water was used throughout.

In a typical synthesis, a mixture of 1.0 mmol $Ce(NO_3)_3$ and 20.0 mmol urea was first uniformly dispersed in 40 mL deionized water with the assistance of ultrasonic radiation at room temperature, in which 0.1 mmol CTAB was added. The obtained solution was refluxed with agitation for 10 h. After rinsing repeatedly and drying at 60 °C, the final product was obtained by calcination at ~500 °C in air for 0.5 h to obtain the desired crystalline and to remove the CTAB [20].

D. Zhang (✉) · L. Shi (✉)
Research Center of Nano Science and Technology,
Shanghai University, Shanghai 200444, China
e-mail: dszhang@shu.edu.cn

L. Shi
e-mail: shiliyi@shu.edu.cn

D. Zhang · L. Huang · J. Zhang · L. Shi
Department of Chemistry, Shanghai University,
Shanghai 200444, China

The samples were observed by a field emission scanning electron microscope (SEM, JEOL JSM-6700F) and a transmission electron microscope (TEM, JEOL JEM-2010F), and the powdered samples were dispersed in absolute ethanol by ultrasonication for 10 min in a KQ-250B ultrasonic bath. X-ray diffraction (XRD) measurements were performed with Rigaku D/MAX-RB X-ray diffractometer by using Cu $K\alpha$ (40 kV, 40 mA) radiation and a secondary beam graphite monochromator.

Results and discussion

The direct evidence of the formation of CeO_2 rhombic microplates was given by SEM and TEM images. Figure 1 shows that the obtained products possess regular rhombic platelike structures with sharp corners and a smooth surface, and the edge length of rhombic plates ranges from 500 nm to 2 μm. The SEM image (Fig. 1b, inset) shows that the thickness of rhombic plates is 100–400 nm. The BET surface area of CeO_2 rhombic microplates is 29.1 m^2/g, which is calculated by nitrogen adsorption–desorption measurements.

The phase of the sample was examined by XRD as shown in Fig. 2. It is confirmed that the obtained ceria rhombic microplates are pure phase products with a face-centered cubic structure according to JCPDS 78-0694. No obvious peaks corresponding to cerium nitrate or other cerium oxides were observed in the powder pattern.

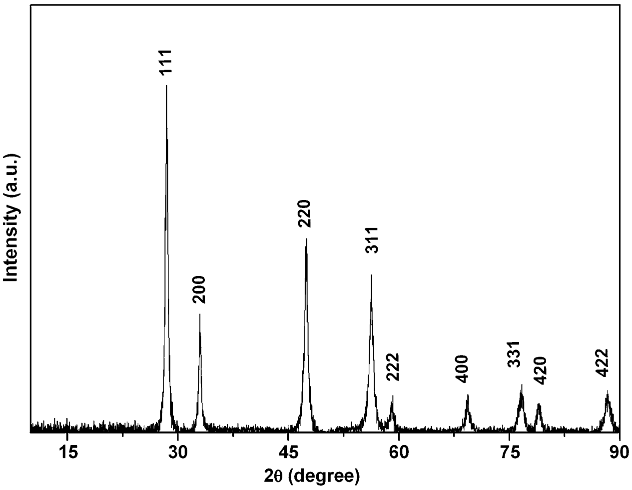

Fig. 2 XRD pattern of CeO_2 rhombic microplates

The formation process of CeO_2 rhombic microplates has also been investigated. In this preparation experiment, the surfactant CTAB plays an important role in the formation of CeO_2 rhombic microplates. When the reaction was carried out without the aid of CTAB, no rhombic microplates but the irregular particles as shown in Fig. 3a. It is noted that these irregular particles are in the range of 500 nm to 2 μm with irregular edges and corners. Figure 3b shows that CeO_2 rhombic microplates are formed with the addition of CTAB, but the size distribution is wide. It is clear that the particle size is becoming uniform with increasing the ratio of CTAB. So it may be suggested

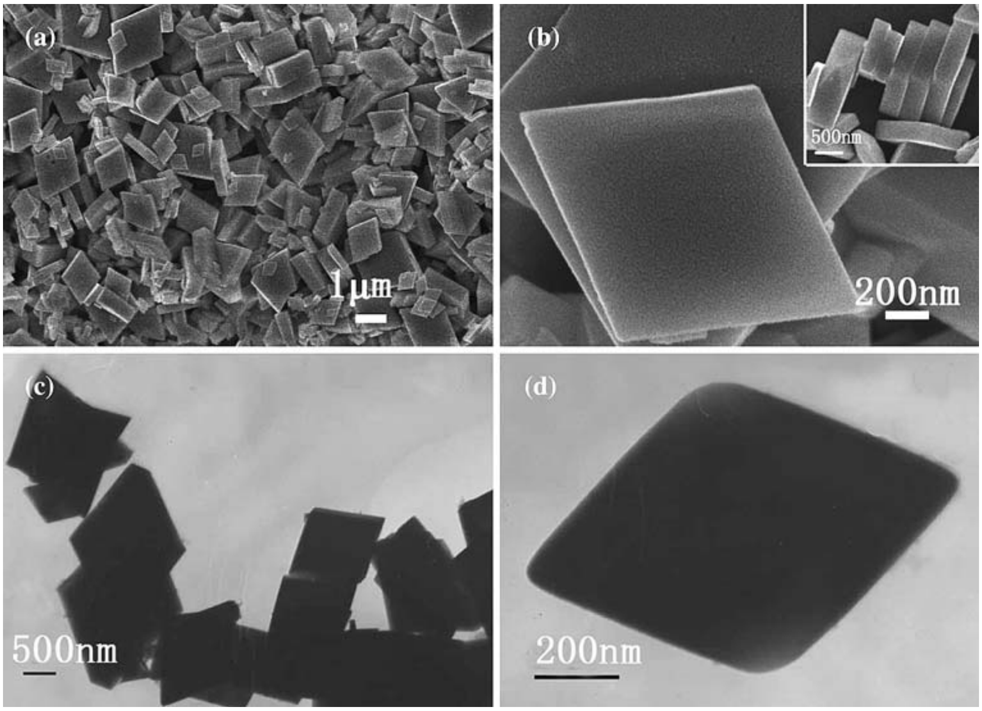

Fig. 1 SEM (**a**, **b**) and TEM (**c**, **d**) images of CeO_2 rhombic microplates

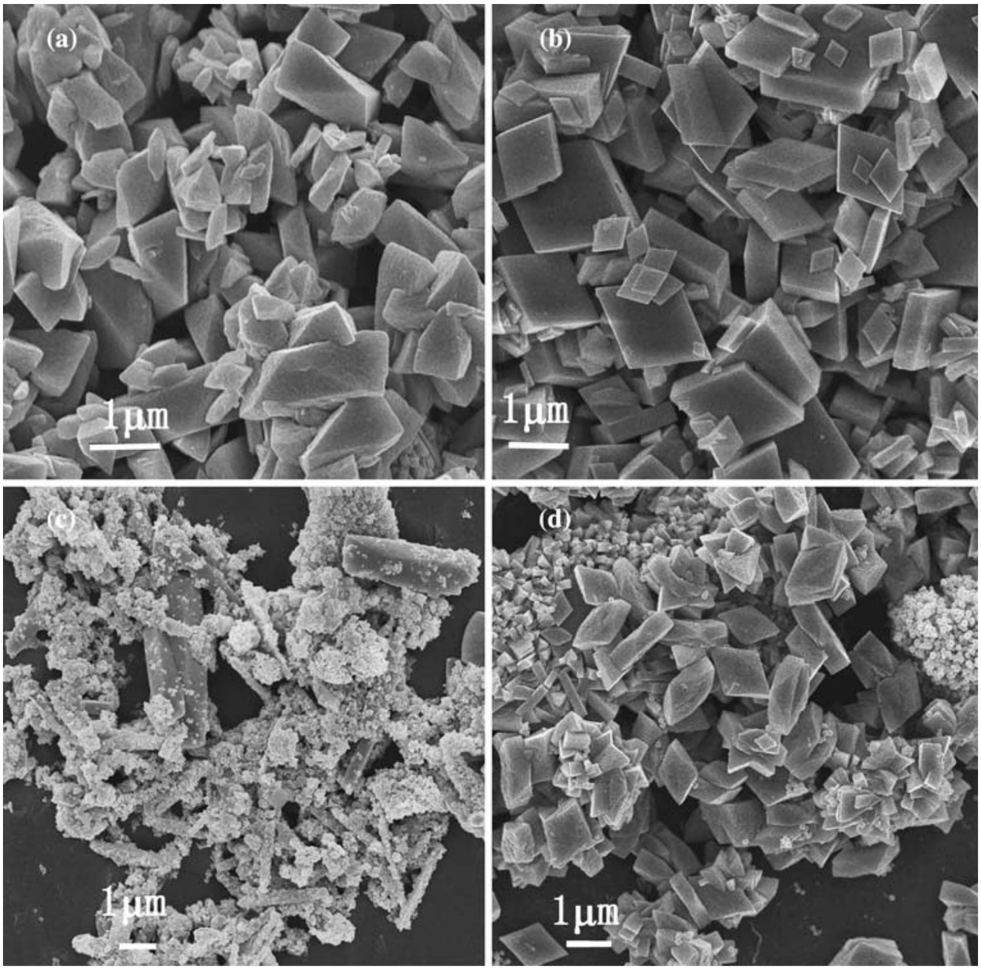

Fig. 3 TEM images of samples (**a**) prepared without CTAB, (**b**) prepared with the addition of CTAB, (**c**) prepared at 60 °C, and (**d**) prepared by reflux for 1 h

that the oriented crystal growth is directed by CTAB, which results in the formation of rhombic microplates. It is found that the reaction temperature and time also play an important role in the formation of rhombic microplates. When the reaction temperature is lower than the boiling point of water (100 °C), the mixture of nanoparticles, nanorods and irregular microrods was observed in the products (Fig. 3c), indicating that the high temperature favors the growth of regular rhombic microplates in the aqueous solution. Similarly, when the reflux time is not enough, some nanoparticles and nanoplates are also observed in the rhombic platelike products (Fig. 3d). It could be concluded that the rhombic microplates may evolve from these nanoparticles, and CTAB plays an assistant role in the evolution.

Conclusions

In summary, for the first time, ceria rhombic microplates were prepared by water reflux techniques with the assistance of CTAB under ambient air. It is found that the obtained ceria rhombic microplates are pure phase products with a face-centered cubic structure with the edge length of 0.5–2 μm and the thickness of 100–400 nm. Such CeO_2 rhombic microplates are very interesting for further studies on their physical and chemical properties. Considering the convenience of the procedure, this surfactant-assisted reflux route is promising and may be extended to fabricate other nanostructures.

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References

1. Teo BK, Sun XH (2007) Chem Rev 107:1454. doi:10.1021/cr030187n
2. Yang HP, Zhang DS, Shi LY, Fang JH (2008) Acta Mater 56:955. doi:10.1016/j.actamat.2007.10.052

3. Balducci G, Islam MS, Kaspar J, Fornasiero P, Graziani M (2000) Chem Mater 12:677. doi:10.1021/cm991089e
4. Wang ZL, Feng X (2003) J Phys Chem B 107:13563. doi:10.1021/jp036815m
5. Feng XD, Sayle DC, Wang ZL, Paras MS, Santora B, Sutorik AC et al (2006) Science 312:1504. doi:10.1126/science.1125767
6. Shchukin DG, Caruso RA (2004) Chem Mater 16:2287. doi:10.1021/cm0497780
7. Gomes J, Serra OA (2008) J Mater Sci 43:546. doi:10.1007/s10853-007-1777-5
8. Mai HX, Sun LD, Zhang YW, Si R, Feng W, Zhang HP et al (2005) J Phys Chem B 109:24380. doi:10.1021/jp055584b
9. Yang S, Gao L (2006) J Am Chem Soc 128:9330. doi:10.1021/ja063359h
10. Ho C, Yu JC, Kwong T, Mak AC, Lai S (2005) Chem Mater 17:4514. doi:10.1021/cm0507967
11. Tang B, Zhuo L, Ge J, Wang G, Shi Z, Niu J (2005) Chem Commun (Camb) 3565. doi:10.1039/b500708a
12. Vantomme A, Yuan ZY, Du GH, Su BL (2005) Langmuir 21:1132. doi:10.1021/la047751p
13. La RJ, Hu ZA, Li HL, Shang XL, Yang YY (2004) Mater Sci Eng A 368:145. doi:10.1016/j.msea.2003.10.279
14. Sun CW, Li H, Wang ZX, Chen LQ, Huang XJ (2004) Chem Lett 33:662. doi:10.1246/cl.2004.662
15. Yang R, Guo L (2005) J Mater Sci 40:1305. doi:10.1007/s10853-005-6958-5
16. Zhang DS, Fu HX, Shi LY, Pan CS, Li Q, Yu WJ (2007) Inorg Chem 46:2446. doi:10.1021/ic061697d
17. Zhang DS, Shi LY, Fu HX, Fang JH (2006) Carbon 44:2853. doi:10.1016/j.carbon.2006.06.012
18. Zhang DS, Fu HX, Shi LY, Fang JH, Li Q (2007) J Solid State Chem 180:654. doi:10.1016/j.jssc.2006.11.025
19. Tang CC, Bando Y, Liu BD, Golberg D (2005) Adv Mater 17:3005. doi:10.1002/adma.200501557
20. Guo Z, Du F, Li G, Cui Z (2006) Inorg Chem 45:4167. doi:10.1021/ic052189r
21. Zhong LS, Hu JS, Cao AM, Liu Q, Song WG, Wan LJ (2007) Chem Mater 19:1648. doi:10.1021/cm062471b
22. Sun CW, Sun J, Xiao GL, Zhang HR, Qiu XP, Li H et al (2006) J Phys Chem B 110:13445. doi:10.1021/jp062179r
23. Pan CS, Zhang DS, Shi LY (2008) J Solid State Chem 181:1298. doi:10.1016/j.jssc.2008.02.011
24. Pan CS, Zhang DS, Shi LY, Fang JH (2008) Eur J Inorg Chem 2429. doi:10.1002/ejic.200800047