Chinese Chemical Letters Vol. 16, No. 8, pp 1109-1112, 2005
http://www.imm.ac.cn/journal/ccl.html

Preparation and Characterization of Three-dimensionally Ordered Crystalline Macroporous CeO_2

Xi Yan ZHANG, Tong Wen WANG*, Wen Qing JIANG,
Di WU, Ling LIU, Ai Hong DUAN

Department of Chemistry, Yunnan Normal University, Kunming 650092

Abstract: A stable 3DOM CeO_2 with well-defined inverse opal microstructure and crystalline walls structure has been successfully synthesized by application of three-dimensional order PMMA beads as templates. Structural feature of products was characterized by using SEM, DTA-TG, XRD.

Keywords: 3DOM, CeO_2, PMMA colloidal crystal template, crystalline wall.

Three-dimensional ordered macroporous (3DOM) materials are of great potential importance in catalysis, selective separation, sensor arrays and communications with optical band gaps[1]. Many results in the synthesis of 3DOM materials have been reported, such as closed-packed silica spheres or polystyrenes (PS) templating routes for silica[2], metal oxides[1-6] and metals[7]. Recently, poly(methyl methacrylate) (PMMA) colloidal crystal templates have been used to prepare 3DOM materials of metals[8], metal alloys[8-9] and sulfated zirconia[10]. Compared with PS, PMMA templates have better wettability with polar solvents (such as H_2O and alcohol) and milder removal conditions[8] and do not need the addition of citrate ions[6]. As a consequence, 3DOM structures could be obtained with an easier process by using PMMA colloidal crystal templates, introducing fewer structural defects. To avoid collapse of pores, the ideal wall of porous materials would be crystalline. Nano-sized cerium dioxide materials are widely used as polishing powder, coating for high temperature, catalyst, optical and ceramic materials[11]. Under some conditions, cerium dioxide shows a molecular preorganization, which supports to form crystals. The above advantages make it accessibility to prepare nano-sized macroporous CeO_2 materials.

Experimental

Non-crossed-linked, monodisperse poly (methyl methacrylate) latex spheres were synthesized at 70°C for 2 h according to literature[12]. Before use, the spheres were close-packed into colloidal crystal by centrifugation for 12 h (1000 r/min) and washed with water and methanol for several times followed by drying at 50 - 60°C for 4 h in vacuum. Then appropriate closed-packed PMMA colloidal crystals were immersed by cerous

* E-mail: wangtw@public.km.yn.cn

nitrates solution ($Ce(NO_3)_3 \cdot 6H_2O$) with alcohol (0.5 mol/L) for 1 min. Excess solution was removed by filtration. The above samples were dried at 50 - 60°C for 30 min in vacuum. Then, the composites were soaked in ammonia solution (2 mol/L) for 3 - 5 min and dried as above. The templates were removed by keeping at 310°C for 3 h and then calcined for 4 h at 350°C, 450°C, 600°C and 800°C, respectively (heating rate, 2°C/min). For comparison, 3DOM SiO_2 materials were prepared with SiO_2 sol (a molar ratio of initial reaction is $Si(OEt)_4$: EtOH : HCl : H_2O = 1.00 : 3.51 : 2.27 : 1.62) by using the same PMMA templates.

Results and Discussion

The centrifuged PMMA spheres (**Figure 1**) formed well-ordered periodic close-packed arrays in a long range. The diameter of the spheres is *ca*. 320-360 nm based on the data obtained by static comparing a large number of spheres in the templates, which shows the diameters of spheres are narrow distributed. It is necessary for stable well-ordered skeletons to control the viscosity and the penetrability of the precursors. In our work, the best concentration of the precursors is 0.5 mol/L and the time of immersion is only 1.0 min. In addition, DTA-TG curves (**Figure 2**) were used to examine the decomposing condition of PMMA/cerium hydroxide in order to let PMMA to decompose slowly and avoid collapse of 3DOM structure.

Figure 1 SEM images of PMMA colloidal crystal templates with different magnification: (a) ×13,400 (b) ×60,000

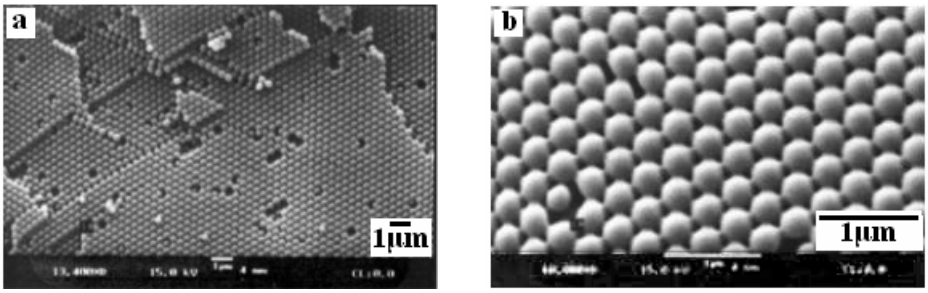


Figure 2 DTA-TG curves of PMMA/cerium hydroxide at a heating rate of 10°C·min^{-1}

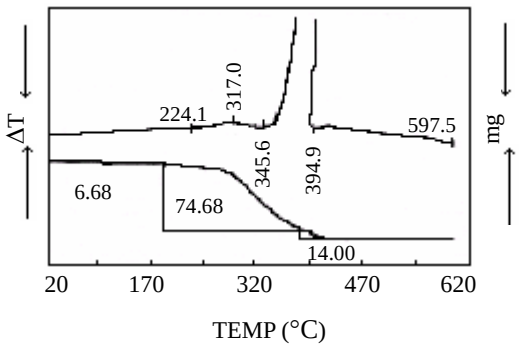


Figure 3(a, b) presents the SEM image of the as-synthesized macroporous ceria after calcinations at 450°C for 4 h. It is seen that the removal of the PMMA templates did not destroy the original ordered structure replicated into ceramic matrix. The interconnected network of the spherical voids left in the ceria was still arranged in well-ordered close-packed structures. The average size of the voids and thickness of the walls are about 200-240 nm and 45-60 nm respectively, and the void size is evidently smaller than that of the PMMA sphere due to shrinkage during calcinations. The thickness of walls of the calcined sample at 800°C (**Figure 3(c)**) is *ca*. 50-70 nm, which suggests that the degree of crystallization for ceria increases with temperature rising. The thicker wall of 3DOM ceria shows that CeO_2 has a lower nucleation rate and is easier to form larger crystalline grains in the walls. Compared with 3DOM SiO_2 with amorphous walls synthesized using the same PMMA template (**Figure 3(d)**), crystalline macroporous CeO_2 materials have less 3D periodicity, which shows that the larger grain size of crystals in 3DOM CeO_2 wall tends to reduce 3D periodicity.

The phases of components in 3DOM CeO_2 can be further identified as cubic crystalline cerium (IV) dioxide by powder XRD characterization (**Figure 4**). Higher temperature leads to better crystal. On the basis of Scherrer equation, the average grain size of 3DOM CeO_2 calcined at 800°C is *ca*. 47 nm.

Figure 3 SEM of 3DOM materials: CeO_2 calcined at 450°C, (a) ×10,300 (b) ×110,000 (c) CeO_2 calcined at 800°C, ×110,000 (d) SiO_2 calcined at 600°C, ×110,000

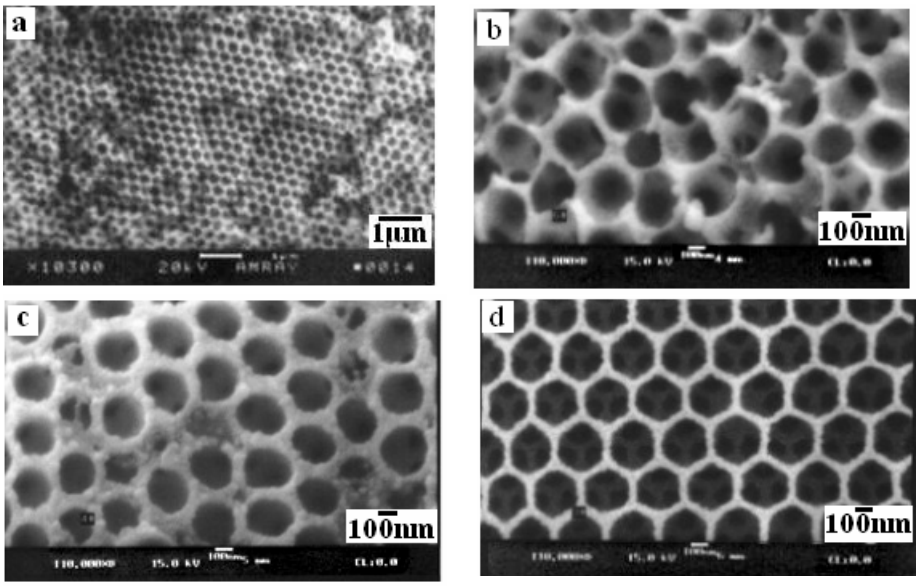
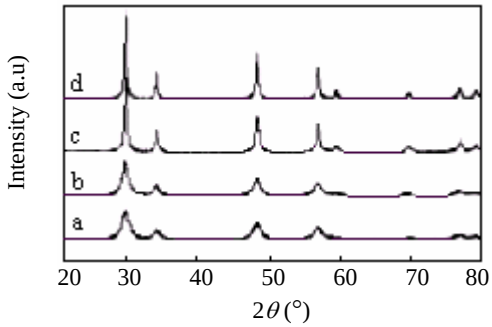


Figure 4 Powder XRD pattern of 3DOM CeO_2 calcined at different temperature for 4 h: (a) 350°C (b) 450°C (c) 600°C (d) 800°C



The present work demonstrates that a stable 3DOM CeO_2 with well-defined inverse opal microstructure and crystalline walls structure has been successfully synthesized by application of three-dimensional order PMMA beads as templates. It has been revealed that the ordered close-packed template, viscosity of the precursors and calcination temperature have important effect on the formation of ordered 3DOM networks, wall thickness and crystallization. By adjusting some conditions, this synthetic procedure may cover oxides of some other rare earth elements. Further research on these elements is underway.

Acknowledgments

The financial supports from The National Natural Science Foundation of China (20163002) and Natural Science Foundation of Yunnan Province (2003E0005Z) are gratefully acknowledged.

References

1. J. E. G. J. Wijnhoven, W. L. Vos., *Science*, **1998**, *281*, 802.
2. B. T. Holland, C. F. Blandford, T. Do, *et al*., *Chem. Mater.*, **1999**, *11*(3), 795.
3. B. T. Holland, C. F. Blandford, A. Stein, *Science*, **1998**, *282*, 538.
4. H. Yan, C. F. Blanford, B.T. Holland, *et al*., *Chem. Mater*., **2000**, *12*, 1134.
5. Y. Shen, Q. Z. Wu, Y. G. Li, *Chinese Journal of Catalysis*, **2002**, *23*(2), 179.
6. Q. Z. Wu, Y. Shen, Y. G. Li, *Acta. Phys-Chim. Sin.*, **2003**, *19*(8), 737.
7. H. Yan, C. F. Blandford, B.T. Holland, *et al*., *Adv. Mater.*, **1999**, *11*, 1003.
8. H. Yan, C. F. Blandford, J. C. Lytle, *et al*., *Chem. Mater.*, **2001**, *13*, 4314.
9. H. Yan, C. F. Blandford, W. H. Smyrl, *et al*., *Chem. Commun*., **2000**, 1477.
10. A. M. Al-Daous, A. Stein, *Chem. Mater.*, **2003**, *15*, 2638.
11. W. P. Hsu, Ronnquist, Matijevice, *Langmuir*, **1988**, *4*(1), 31.
12. D. Zou, S. Ma, R. Guan, *et al*., *Polym. Sci. A: Polym. Chem.*, **1992**, *30*, 137.

Received 27 September, 2004