J Mater Sci (2008) 43:1730–1733
DOI 10.1007/s10853-007-1832-2

Preparation and characterization of ZrO_2 porous nanosolid and its composite fluorescent materials

Xiulin Liu · Deliang Cui · Yan Li · Ying Guo

Received: 2 August 2006 / Accepted: 8 May 2007 / Published online: 11 January 2008

Abstract ZrO_2 porous nanosolid has been successfully prepared by a novel hydrothermal hot-press (HHP) method, using ZrO_2 nanoparticles as the starting material. Furthermore, a kind of O, O-donating chelating regent, morin was assembled into the pores of ZrO_2 porous nanosolids, and a morin/ZrO_2 porous nanocomposite was obtained. Because of the interaction between morin molecules and the surface of ZrO_2 porous nanosolid, a blue-shift of the photoluminescence (PL) peak was observed in ZrO_2/morin nanocomposite by comparing with that of morin.

Introduction

As an excellent structural material, both the preparation and properties of ZrO_2 have been extensively and intensively investigated. For example, when combined with Al_2O_3, a high wear resistance ZrO_2/Al_2O_3 composite material can be prepared [1]. Besides, hydroxyapatite-ZrO_2 composite is a high strength biological material [2, 3], etc. On the other hand, because of the excellent catalytic properties, porous ZrO_2 has attracted considerable attentions in recent years [4–8]. It has been reported that, mesoporous ZrO_2 has been successfully prepared by many kinds of methods, such as carbon dioxide supercritical drying method [5], surfactant-controlled condensation method [6, 7], etc.

Although many kinds of luminescent materials have been prepared by assembling dye molecules into the pores of porous materials, such as porous silicon [9, 10], porous alumina [11, 12], etc, we have not found any reports on the synthesis of functional materials by assembling functional molecules into the pores of porous ZrO_2. To our best knowledge, there is no paper reported the preparation of ZrO_2 porous nanosolids and the related fluorescent materials. In fact, the ZrO_2 porous nanosolid is a new intermediate state between nanopowders and nanoceramics, and it is a solid constructed of nanoparticles forming pores and channels, thus possessing both the high reactivity of nanoparticles and the ideal strength of nanoceramics. Besides, the pores, with the diameter size of several nanometers, may impose a strong quantum confinement effect on the molecules in it, results in the change of the properties of these molecules. This phenomenon will provide us more possibilities of developing new composite functional materials. More recently [13], we reported the successful preparation of ZrO_2 nanoparticles/morin composites by a simple heat refluxing method [14], using ZrO_2 nanoparticles and morin particles as the starting materials, and the phenomenon of PL enhancement was observed. On the basis of above consideration, we have assembled morin molecules into the pores of ZrO_2 porous nanosolid, and the ZrO_2/morin composite fluorescent materials have been successfully prepared.

Experimental

Preparation of ZrO_2 porous nanosolid

ZrO_2 bulk porous nanosolid was prepared as follows: An aliquot of 4.5 g ZrO_2 nanoparticles (with average particle

X. Liu (✉) · Y. Li · Y. Guo
College of Science, Civil Aviation University of China,
Tianjin 300300, P.R. China
e-mail: luckyliuxiulin@yahoo.com.cn

D. Cui
State Key Laboratory of Crystal Materials,
Shandong University, Jinan 250100, China

size of 20 nm, and purchased from Mingri Nanometer Materials Co. Ltd., China) were added to a beaker at first, then an aliquot of 50 mL water was added into the beaker. After stirring for 10 min, the samples were filtered with a membrane (the average pore size is 0.45 μm) to remove the excessive water. Finally, the wet ZrO_2 nanoparticles were quickly mounted into a HHP autoclave (see Fig. 1). Then the autoclave was applied with a constant pressure of 90 MPa. At the same time, the temperature was increased to 200 °C with the rising speed of 1.5 °C/min and kept constant for 180 min. After the autoclave was cooled to room temperature, ZrO_2 porous nanosolids were obtained. They were all dried in an oven for 8 h at 50 °C before assembling.

Preparation of ZrO_2/morin porous nanocomposites

The ZrO_2/morin porous nanocomposites were prepared by using an apparatus shown in Fig. 2. During the process of assembling, container 1 was kept constant at atmospheric pressure, whereas container 2 was pumped to a lower pressure, and then a pressure difference between container 1 and 2 was maintained. Under this pressure difference, morin (its molecule structure is shown in Fig. 3, and purchased from E. Merck, Darmstadt) anhydrous alcohol solution was driven to flow into the container 2 by passing through the pores of ZrO_2 porous nanosolids. During this process, morin molecules were adsorbed on the surface of the pores, and at the same time, chemical bonds formed between the morin molecules and the surface atoms of the pores, as a result, ZrO_2/morin porous nanocomposites were obtained.

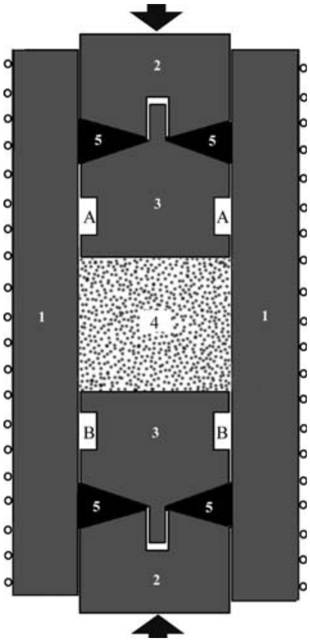


Fig. 1 Schematic structure of hydrothermal hot-press autoclave (1) cylinder, (2) outer-piston, (3) inner-piston, (4) sample and (5) Teflon ring

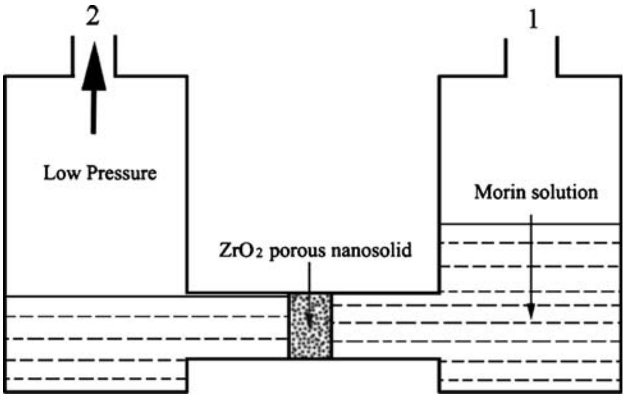


Fig. 2 Apparatus used for preparing ZrO_2/morin porous nanocomposite

In our experiment, the morin concentrations were kept at 3.0×10^{-3} mol/L, and the assembling time was 12, 24, 36, 48 and 60 h, respectively. After the assembling process completed, all the samples were washed by alcohol for several times to remove the unbound morin molecules.

All the samples were dried in an oven at 50 °C for 6 h before characterization.

Characterization

The photoluminescence spectra of the samples were obtained with a FLS 920 fluorescent spectrometer. The pore size distribution of the samples was examined on a Pore Master-60 mercury intrusion porosimetry. The FTIR spectra were collected on a NEXUS-670 spectrometer with the spectral resolution of 4.00 cm^{-1}. The samples were mixed with KBr with weight ratio of sample: KBr of 1:100 and pressed into pellet for characterization. All measurements were carried out at room temperature.

Results and discussion

During the hydrothermal hot press treatment, the ZrO_2 nanoparticles connected with each other. At the same time, large amount of small pores or channels appeared when water escaped from the sample, then a bulk ZrO_2 porous nanosolid was obtained. Figure 4 shows the SEM photograph of the bulk ZrO_2 porous nanosolid. It can be seen that, there are many small round pores or channels distributed uniformly in the sample.

As a key parameter of bulk ZrO_2 porous nanosolids, the pore radius distribution is shown in Fig. 5. Obviously, the size of most pores distributed in the range of 3–13 nm, and

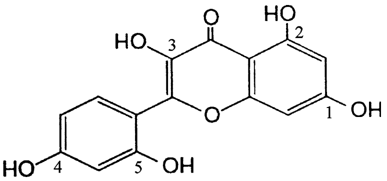


Fig. 3 Schematic drawing of morin molecule

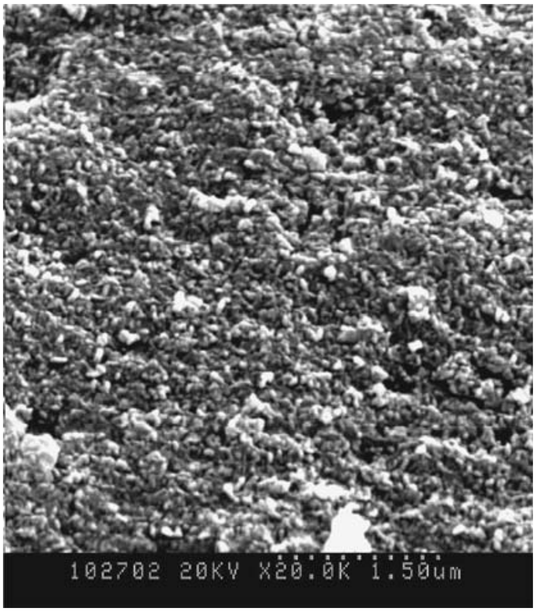
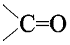
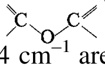
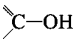


Fig. 4 SEM photograph of the bulk ZrO_2 porous nanosolid

the pores are rather large compared with the size of morin molecules, so morin molecules can easily be assembled into the pores.

Figure 6 presents the FTIR spectra of ZrO_2 porous nanosolids, morin and ZrO_2/morin porous nanocomposites. From this figure, it is known that, the major absorption peaks of ZrO_2 porous nanosolids locate at 1,631 cm^{-1} (attributed to H_2O), 1,450, 1,405 cm^{-1} (attributed to CO_3^-) and 1,384 cm^{-1} (attributed to NO_3^-) (as shown in Fig. 6a). Whereas, the peaks of morin molecules at 1,652, 1,508 and 1,246 cm^{-1} in Fig. 6e can be attributed to the stretch vibration mode of C=O in  group, vibration of C=C in benzene rings and asymmetry stretch vibration of C–O–C in  group, respectively. The peaks at 1,204 and 1,174 cm^{-1} are attributed to the stretch vibration of C–O in 1, 2, 3, 4, 5  groups (as shown in Fig. 3). The other peaks at 1,606, 1,572, 1,469, 1,450 cm^{-1} can be attributed to the C=C on benzene rings, and those at 1,352, 1,327 and 1,308 cm^{-1} come from the absorption of OH groups [15]. From these spectra we can see that, the peaks at 1,246 and 1,174 cm^{-1}, which are attributed to morin, shift to 1,239 and 1,182 cm^{-1} respectively in the composites. This result reveals that morin molecules not only enter into ZrO_2 porous nanosolids, but also are chemically bound on the surface of the pores of ZrO_2 porous nanosolids.

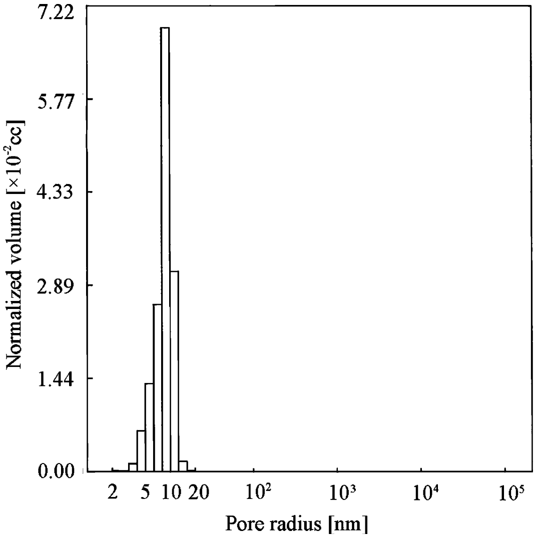


Fig. 5 Pore radius distribution of bulk ZrO_2 porous nanosolids

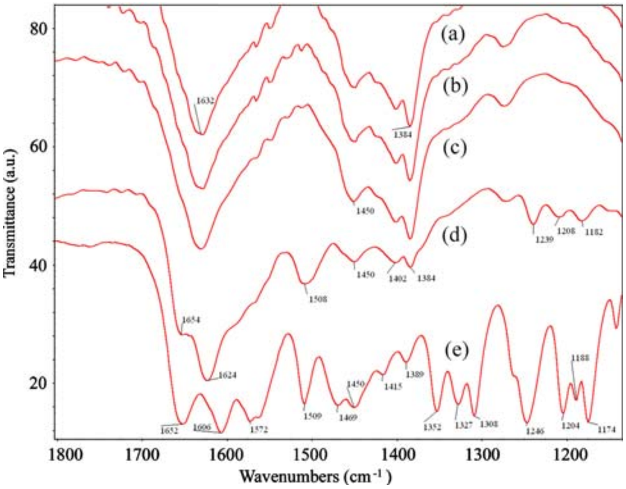


Fig. 6 FTIR spectra of ZrO_2 porous nanosolids, morin and composites (**a**) ZrO_2 porous nanosolids, (**b**) composite prepared by assembling 36 h, (**c**) composite prepared by assembling 48 h, (**d**) composite prepared by assembling 60 h and (**e**) morin

Figures 7 and 8 present the PL spectra of morin solution (3.0×10^{-3} mol/L) and ZrO_2/morin porous nanocomposites under the excitation of 450 nm. In Fig. 8, with the prolonging of the assembling time, the PL intensity increases at first and followed by a decrease. By comparing Figs. 7 and 8, it is found that the PL peak of morin shifted from 556 nm to 530 nm after being assembled into the pores of ZrO_2 porous nanosolids. The reason for this blue-shift phenomenon may be that, the morin molecules interact with the surface atoms of ZrO_2 porous nanosolids, which have been revealed by the FTIR spectra. Further

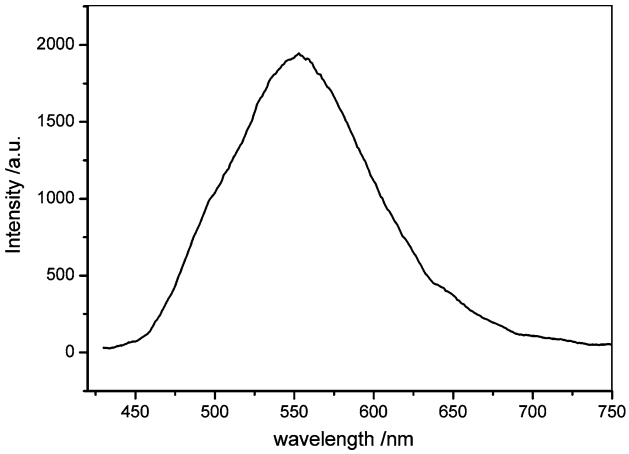


Fig. 7 The PL spectrum of morin solution (3.0×10^{-3} mol/L)

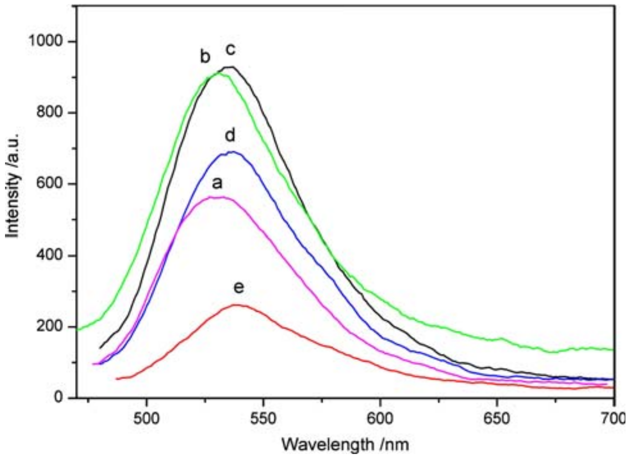


Fig. 8 The PL spectra of ZrO_2/morin nanocomposites with different assembling time (**a**) 12 h, (**b**) 24 h, (**c**) 36 h, (**d**) 48 h and (**e**) 60 h

works that required for the full understanding of the mechanism are being conducted.

Conclusions

By using the hydrothermal hot-press method, ZrO_2 porous nanosolids can be prepared, using ZrO_2 nanoparticles as the starting material. Furthermore, this porous nanosolid has been used as the precursor for synthesizing ZrO_2 porous nanosolids/morin composite fluorescent materials by assembling morin into its pores. Because of interaction between the morin molecules and the surface of ZrO_2 porous nanosolid, a blue shift of the PL peak was observed in the composite materials compared with that of morin.

Acknowledgement This project is jointly supported by National Natural Science Foundation of China (Contract No. 90206042), Natural Science Foundation of Tianjin (No. 043602911, 05yfJMTC 12900) and Science Foundation of CAUC (05qd06q).

References

1. Kerkwijk B, Mulder E, Verweij H (1999) Adv Eng Mater 1:69
2. Silva VV, Lameiras FS, Lobato ZIP (2002) J Biomed Mater Res 63:583
3. Shen ZJ, Adolfsson E, Nygren M, Gao L, Kawaoka H, Niihara K (2001) Adv Mater 13:214
4. Valéro R, Durand B., Guth J-L, Chopin T (1999) Micro Meso Mater 29:311
5. Suh DJ, Park TJ (2002) Chem Mater 14:1452
6. Schüth F, Ciesla U, Schacht S, Thieme M, Huo Q, Stucky G (1999) Mater Res Bull 34:483
7. Wong MS, Ying JY (1998) Chem Mater 10:2067
8. Schattka JH, Shahukin DG, JIia J, Antonietti M, Caruso RA (2002) Chem Mater 14:5103
9. Canham LT (1993) Appl Phys Lett 63:337
10. Elhouichet H, Oueslati M (2001) Mat Sci Eng B79:27
11. Zhao Y, Yang D, Zhou C, Yang Q, Que D (2003) J Lumin 105:57
12. Jia RP, Shen Y, Luo HQ, Chen XG, Xue ZD (2004) Solid Stat Commun 130:367
13. Liu X, Li Y, Wang X (2006) Mater Lett 60:1943
14. Liu X, Cui D, Wang Q, Xu H, Li M (2005) J Mater Sci 40:1111
15. Xie JX (1987) Applications of infrared spectroscopy in organic chemistry and drug chemistry. Science Press, Beijing, pp 41–330 (in Chinese)