Chemistry Letters Vol.35, No.10 (2006)

Microwave-assisted Fabrication and Characterization of $BaCO_3$ Nanorods

Ming-Guo Ma,[1,2] Ying-Jie Zhu,*[1] Jie-Fang Zhu,[1] and Guo-Feng Cheng[1]
[1]*Biomaterials and Tissue Engineering Research Center, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing, P. R. China*

(Received July 6, 2006; CL-060767; E-mail: y.j.zhu@mail.sic.ac.cn)

$BaCO_3$ nanorods have been successfully prepared by the microwave-assisted method at 90 °C using $Ba(NO_3)_2$ and $(NH_4)_2CO_3$ in the presence of NaOH or hexamethylenetetramine ($(CH_2)_6N_4$) in ethylene glycol. The heating time and type of alkali played an important role in the size and morphology of $BaCO_3$.

Recently, the biomimetic synthesis and biomineralization process of the biominerals in natural systems have attracted a wide attention.[1] Calcium carbonate, a typical biomineral that is abundant in both organisms and nature, has been widely studied.[2,3] Since the discovery of carbon nanotubes,[4] one-dimensional (1-D) nanostructures have received intense attention because of their potential applications.[5,6] Barium carbonate ($BaCO_3$) is an important material used in the production of glasses and ceramics industry.[7] However, there have been only a few reports on the fabrication of nanostructured $BaCO_3$.[8–14] For example, Qi et al.[10] reported the fabrication of $BaCO_3$ nanowires by using $BaCl_2 \cdot 2H_2O$, Na_2CO_3 in the reverse micelles of $C_{12}E_4$ (tetraethylene glycol monododecyl ether) in cyclohexane. $BaCO_3$ nanowires prepared by using $BaCl_2 \cdot 2H_2O$, Na_2CO_3 in Triton X-100/cyclohexane/water system were also reported.[11]

To develop simple, fast, and low-cost synthesis methods for the control over the morphology of $BaCO_3$ is of great importance for broadening and improving their applications. Microwave heating is a promising technology whose application in synthesis of nanomaterials has been a fast growing area.[15–17] The main advantages of microwave heating are rapid volumetric heating, fast reaction rate, short reaction time, high reaction selectivity, and energy saving. However, there have been only a few reports on the microwave-assisted synthesis of carbonates despite these advantages.[18,19]

In this paper, we have developed a new microwave-assisted route to the controlled synthesis of $BaCO_3$ nanorods using $Ba(NO_3)_2$ and $(NH_4)_2CO_3$ in the presence of NaOH or hexamethylenetetramine ($(CH_2)_6N_4$) in ethylene glycol (EG).

All chemicals were analytical grade reagents and used as received without further purification. In a typical experiment, barium nitrate ($Ba(NO_3)_2$) (0.261 g) and ammonium carbonate ($(NH_4)_2CO_3$) (0.096 g) were dissolved in EG (20 mL) in a flask under magnetic stirring. Hexamethylenetetramine ($(CH_2)_6N_4$, HMT, 0.140 g), or NaOH (0.150 g) was added into the solution. The flask containing the solution was heated to 90 °C and kept at this temperature for 40 min by microwave heating. The product was separated from the solution by centrifugation, washed with absolute ethanol three times, and dried in vacuum. The microwave oven used was a focused single-mode microwave synthesis system (2.45 GHz, Discover, CEM, U.S.A.), which was equipped with a magnetic stirring system and a water-cooled condenser.

X-ray powder diffraction (XRD) patterns were recorded using a D/max 2550 V X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å) and a graphite monochromator, operating at 40 kV and 200 mA. Scanning electron microscopy (SEM) micrographs were recorded with a JSM-6700F field-emission scanning electron microscope. All samples were Au-coated prior to the examination by SEM.

Figure 1 shows XRD patterns of two typical samples synthesized in EG by microwave heating at 90 °C for 40 min in the presence of NaOH and HMT, respectively. Both samples consisted of a well-crystallized single phase of $BaCO_3$ with an orthorhombic structure (JCPDS 71-2394).

The morphologies of the samples were investigated by SEM. Figure 2a shows SEM micrograph of the sample synthesized by microwave heating in the presence of a strong alkali NaOH at 90 °C for 40 min in EG, from which one can see $BaCO_3$ nanorods assembled from nanoparticles. $BaCO_3$ nanorods had relatively uniform sizes with the diameters of about 200 nm and the lengths of about 450 nm. We propose that the growth mechanism of $BaCO_3$ nanorods assembled from nanoparticles follows the oriented attachment mechanism.[20,21] The self-assembly of nanoparticles depend on the interparticle interactions, particle size distribution and particle shape.[22–24] The oriented attachment-based self-assembly was also reported for other inorganic nanoparticles.[25]

The influence of the weak alkalescent additive (HMT) on the morphology of $BaCO_3$ was also investigated (Figure 2b), from which one can see nanorods with a hexagonal cross section.

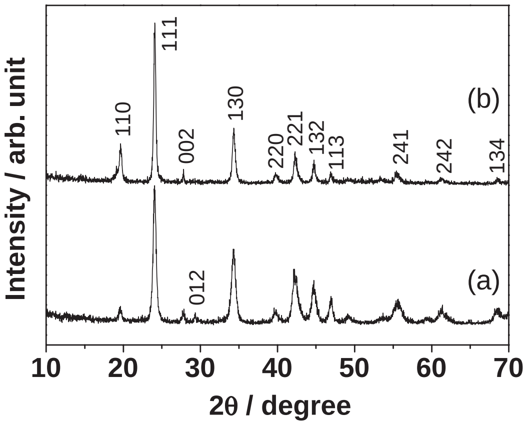

Figure 1. The typical XRD patterns of $BaCO_3$ powders prepared by microwave heating in EG at 90 °C for 40 min: (a) using NaOH, (b) using HMT.

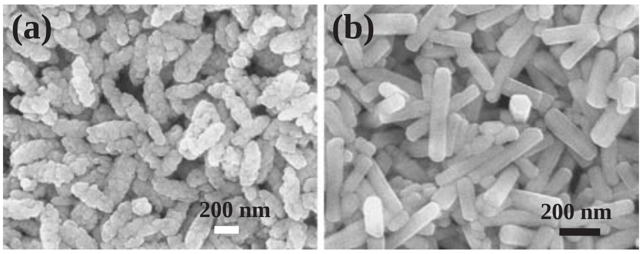

Figure 2. SEM micrographs of $BaCO_3$ prepared by microwave heating at 90 °C for 40 min in EG: (a) using NaOH, (b) using HMT.

This indicates that the alkali has a significant influence on the morphology of $BaCO_3$. $BaCO_3$ nanoparticles formed and self-assembled into nanorods in the presence of a strong alkali NaOH. However, nanorods with a hexagonal cross section were obtained when using a weak alkali HMT.

The heating method also had an influence on the morphology of $BaCO_3$. The aggregates of irregular nanoparticles were formed in the presence of NaOH by heating in an oil bath, in contrast to the nanorods assembled from $BaCO_3$ nanoparticles prepared by the microwave heating. However, the needles with two sharp ends were produced in the presence of HMT by heating in the oil bath.

The effect of the microwave heating time on the product was investigated. In the presence of NaOH, irregular nanoparticle congeries of $BaCO_3$ were observed when the heating time was 5 min (Figure 3a), and the degree of assembly was low. When the heating time was increased to 20 min, $BaCO_3$ nanorods assembled from nanoparticles formed (Figure 3b). The degree of assembly increased with increasing heating time. From Figures 3a, 3b, and 2a, one can clearly see the evolution process of $BaCO_3$ nanorods assembled from nanoparticles.

When using HMT instead of NaOH as an alkali additive, the similar phenomenon was observed. When the heating time was 5 min, the nanorods with tip ends were observed (Figure 3c). The hexagonal outline was observed at central part of the nanorod in a few cases. When the heating time was increased to 20 min, although hexagonal nanorods were commonly observed, some nanoparticles were seen on the top of the nanorods (Figure 3d). When the heating time was increased to 40 min, nanorods with a regularly shaped hexagonal cross section were obtained (Figure 2b).

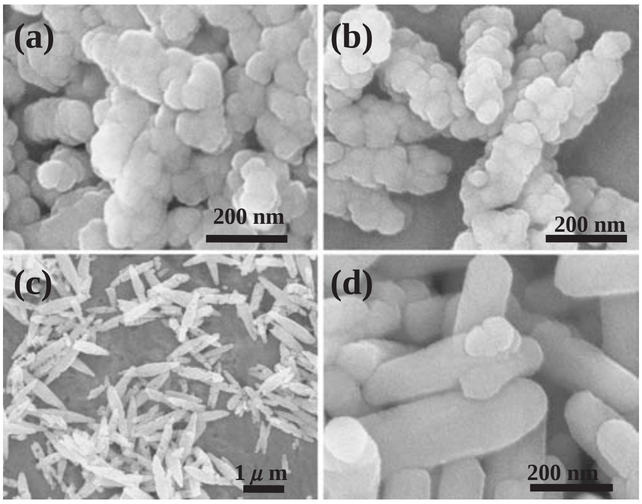

Figure 3. SEM micrographs of $BaCO_3$ prepared by microwave heating in EG at 90 °C using NaOH (a), (b) and HMT (c), (d) for 5 min (a), (c) and 20 min (b), (d).

In summary, the microwave-assisted method has been successfully used for the fabrication of $BaCO_3$ nanorods in EG. The heating time and type of alkali played an important role in the size and morphology of $BaCO_3$. This method is simple, fast, low-cost and suitable for large-scale production of $BaCO_3$ nanorods.

Financial supports from the National Natural Science Foundation of China (No. 50472014), the Chinese Academy of Sciences under the Program for Recruiting Outstanding Overseas Chinese (the Hundred Talents Program), the Fund for Innovation Research from Shanghai Institute of Ceramics, the Opening Project (No. SKL200506SIC) of State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai Postdoctoral Scientific Program (No. 05R214148) are gratefully acknowledged.

References

1 S. Weiner, L. Addadi, *J. Mater. Chem.* **1997**, *7*, 689.
2 H. Cölfen, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 23.
3 K. Naka, Y. Chujo, *Chem. Mater.* **2001**, *13*, 3245.
4 S. Iijima, *Nature* **1991**, *354*, 56.
5 S. Frank, P. Poncharal, Z. L. Wang, W. A. de Heer, *Science* **1998**, *280*, 1744.
6 X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, C. M. Lieber, *Nature* **2001**, *409*, 66.
7 B. Gutmann, A. Chalup, *Am. Ceram. Soc. Bull.* **2000**, *79*, 63.
8 S. H. Yu, H. Cölfen, A. W. Xu, W. F. Dong, *Cryst. Growth Des.* **2004**, *4*, 33.
9 S. H. Yu, H. Cölfen, K. Tauer, M. Antonietti, *Nat. Mater.* **2005**, *4*, 51.
10 L. M. Qi, J. M. Ma, H. M. Cheng, Z. G. Zhao, *J. Phys. Chem. B* **1997**, *101*, 3460.
11 D. B. Kuang, A. W. Xu, Y. P. Fang, H. D. Ou, H. Q. Liu, *J. Cryst. Growth* **2002**, *244*, 379.
12 I. Sondi, E. Matijevic, *Chem. Mater.* **2003**, *15*, 1322.
13 L. L. Li, Y. Chu, Y. Liu, L. H. Dong, L. Huo, F. Y. Yang, *Mater. Lett.* **2006**, *60*, 2138.
14 N. W. Zheng, Q. S. Wu, Y. P. Ding, Y. D. Li, *Chem. Lett.* **2000**, 638.
15 Y. J. Zhu, W. W. Wang, R. J. Qi, X. L. Hu, *Angew. Chem., Int. Ed.* **2004**, *43*, 1410.
16 W. Y. Yu, W. X. Tu, H. F. Liu, *Langmuir* **1999**, *15*, 6.
17 M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa, T. Tsuji, *Chem. Eur. J.* **2005**, *11*, 440.
18 R. Rodríguez-Clemente, J. Gómez-Morales, *J. Cryst. Growth* **1996**, *169*, 339.
19 R. J. Qi, Y. J. Zhu, *J. Phys. Chem. B* **2006**, *110*, 8302.
20 R. L. Penn, J. F. Banfield, *Geochim. Cosmochim. Acta* **1999**, *63*, 1549.
21 R. L. Penn, J. F. Banfield, *Science* **1998**, *281*, 969.
22 C. P. Collier, T. Vossmeyer, J. R. Heath, *Annu. Rev. Phys. Chem.* **1998**, *49*, 371.
23 M. P. Pileni, *J. Phys. Chem. B* **2001**, *105*, 3358.
24 M. Li, H. Schnablegger, S. Mann, *Nature* **1999**, *402*, 393.
25 C. Pacholski, A. Kornowski, H. Weller, *Angew. Chem., Int. Ed.* **2002**, *41*, 1188.