Synthesis of Wollastonite Single Crystal Nanowires by a Novel Hydrothermal Route

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This article firstly reports the successful synthesis of wollastonite single crystal nanowires by hydrothermal route. We obtained xonotlite nanowires on hydrothermal condition at a lower temperature (180 °C) using cationic surfactant as template. The nanowires have high aspect ratios more than 100 with diameters of 50–100 nm. After calcination at 800 °C for 2 h, xonotlite nanowires transformed to wollastonite and the fibrous structure was preserved. They were characterized by powder X-ray diffractometry (XRD), transmission electron microscopy (TEM). The mechanism of wollastonite nanowires formation was also discussed.

Because of their promise as advanced materials and in advanced technologies, one-dimensional nanoscale building blocks, such as nanotubes, nanowires, and nanorods with uniform sizes and aspect ratios, have been intensively explored. The preparation of nanowires from cheap and commonly available materials is of interest as such nanowires might find applications in fabricating nanodevices and in nanoscale electronic transportation, and could be used as an additive of nanostructured materials to improve material properties on the basis of their structures and properties.

Wollastonite, a raw material mainly used for traditional ceramics,[1] is also a candidate material for high-frequency insulator owning to its low dielectric loss at high frequency.[2] Recently, wollastonite (β-$CaSiO_3$) ceramics have been studied as bioactive materials for orthopaedic applications because of its good bioactivity and biocompatibility.[3–5] In addition, wollastonite powders have been used as polymer filler for preparation of composite and the results showed that the incorporation of wollastonite could improve the mechanical properties[6] and bioactivities of the composites.[7] The processing of granular powders and its bulk materials have been studied,[8,9] but related nanowires have not been reported so far.

In previous study, some researchers had synthesized xonotlite microfibers from suspension of silica and $Ca(OH)_2$ by hydrothermal method, and high reaction temperature (250–350 °C) was needed in their experiments.[10,11] It is well known that xonotlite transforms to wollastonite by heating.[12] In our study, we successfully synthesized xonotlite nanowires using tetraethyl orthosilicate (TEOS) as Si source, newly synthesized $Ca(OH)_2$ as Ca supplier which is highly reactive, and cationic surfactant as the template by hydrothermal treatment at a lower temperature (180 °C). After calcination at 800 °C for 2 h, the xonotlite nanowires were thoroughly transformed to wollastonite nanowires.

The procedure employed for the synthesis of wollastonite nanowires is as follows. 0.3 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 60-mL of distilled water and 4 mL of TEOS was added, the solution was stirred for 5 min using a magnetic stirrer and then dispersed by ultrasonic until TEOS/water emulsion formed. 3.68 g of $Ca(NO_3)_2 \cdot 4H_2O$ and 1.24 g of NaOH were dissolved in 20 mL of distilled water, respectively. NaOH solution was then dropped into $Ca(NO_3)_2$ solution to obtain $Ca(OH)_2$ suspension. The $Ca(OH)_2$ suspension was homogenously mixed with the TEOS/water emulsion. The pH of the final suspension is 11.8 and the Ca/Si ratio is 1.0. The suspension was transferred into stainless steel autoclaves, heated at 180 °C for 30 h, followed by cooling to room temperature on standing. After the hydrothermal reaction, the obtained suspension was filtrated and washed with distilled water and anhydrous ethanol for three times, respectively. The resultant powders were dried at 60 °C for 72 h. For preparation of wollastonite nanowires, the powders were then calcined at 800 °C for 2 h in a muffle furnace.

The powders before and after calcination were characterized by X-ray diffraction (XRD) with a Japan Rigaku D/max 2550V X-ray diffractometer with monochromated Cu Kα radiation ($\lambda = 0.154178$ nm). A scan rate of $0.02\,s^{-1}$ was applied to record the patterns in the 2θ range of 20–60°. The morphology and sizes of the powders before and after calcination were characterized by transmission electron microscopy (TEM) on a JEM2010.

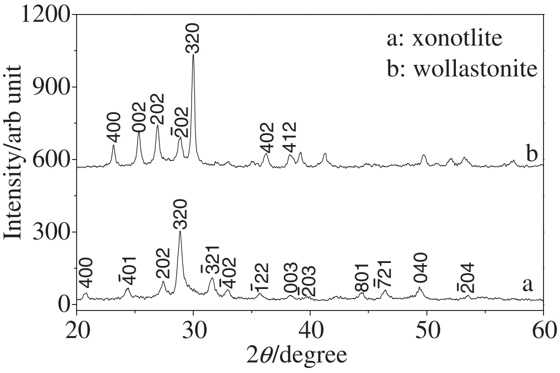

Figure 1. XRD pattern of the (a) xonotlite and (b) wollastonite nanowires.

Figure 1a showed the XRD patterns of the powders before calcination. They were identified as xonotlite (Figure 1a, JCPDS card: No. 23-0125). It could be seen that there were numerous sharp peaks and low background in the XRD pattern of the xonotlite nanowires. The TEM image (Figure 2a) indicated that the xonotlite nanowires had a smooth surface and a fiber-like shape, 50–100 nm in diameter and 10–15 μm in length.

TEOS is highly reactive, it could quickly hydrolyze under catalysis of OH^-:

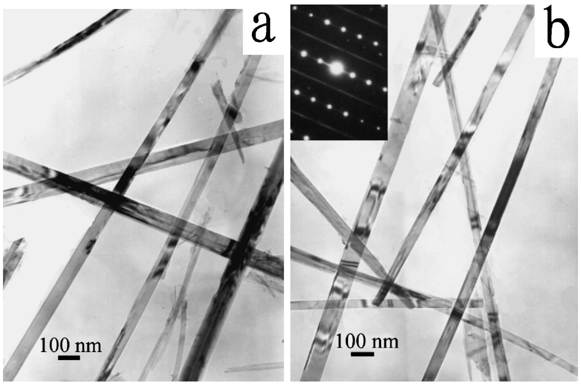

Figure 2. TEM images of the (a) xonotlite and (b) wollastonite nanowires with SAD pattern.

$$(C_2H_5)_4SiO_4 + 4H_2O \rightarrow 4C_2H_5OH + H_4SiO_4$$
$$H_4SiO_4 + 2OH^- \rightarrow SiO_3{}^{2-} + 3H_2O$$

The newly synthesized $Ca(OH)_2$ is also highly reactive, it affords the Ca^{2+} for the synthesis of xonotlite. The high reactivity of the raw materials afford the possibility of the reaction under relatively lower temperature by lowing the activation energy.

As for the effect of CTAB, one is the emulsification in TEOS/water system which facilitates the homogenously mixing of the raw materials. In addition, CTAB can inhibit the excess aggregation of nanowires through its adsorption on the surface of the nanowires. But the most important is, similar to other surfactant, that CTAB was thought to be able to act as a template.[13] CTAB is a cationic surfactant and its critical micelle concentration (cmc) is 0.03% (0.9–1.0 mM).[14] Above the cmc, transition from spherical micelles to rod-like micelles occurred, and the size of micelles increased with the increase of CTAB concentration, eventually resulting in long, flexible wormlike micelles.[15] In our system, with CTAB concentration of 0.3%, CTAB could easily form rod-like micelles.

According to the studies by Yao and Xiong,[16,17] the formation of xonotlite might be explained as the following: firstly, the CTAB formed rod-like micelles in which TEOS oil phase was enwrapped. Because of the concentration difference between the inside (TOES oil phase) and outside (water phase) of the rod-like micelles, the $SiO_3{}^{2-}$ transferred to the surface of the micelles and CTAB–$SiO_3{}^{2-}$ rod-like micelles formed. In the presence of Ca^{2+}, calcium silicate hydrate clusters were preferentially condensed on the rod-like micellar surface. The micelles act as nucleating sites for the growth of xonotlite crystals. During the hydrothermal stage, CTAB–xonotlite complexes formed and coalesced to form a stable three-dimensional fibrous structure.

After calcination at 800 °C for 2 h, the phase of the powders transformed from xonotlite to wollastonite, which was identified by XRD (Figure 1b, JCPDS card: No. 43-1460). It can be seen that the sharp peaks with minor diffuse background represented crystalline wollastonite. Meanwhile, the XRD pattern of the sample did not reveal any other phase than wollastonite. From the TEM image (Figure 2b) of the calcined powders, it can be seen that the original shapes and sizes of xonotlite nanowires were still preserved, which could be attributed to the similar crystal structure between xonotlite and wollastonite. The inset indicates its electron diffraction pattern (SAD), which demonstrates that the wollastonite nanowires were composed of single crystal.

Wollastonite single crystal nanowires have been successfully synthesized by hydrothermal route. After the hydrothermal reaction, xonotlite nanowires were firstly obtained. After calcination at 800 °C for 2 h, the xonotlite nanowires were thoroughly transformed to wollastonite, preserving the fibrous structure. The resultant wollastonite nanowires had a diameter of 50–100 nm, and a length of up to 10–15 µm. This is the first report about the synthesis of wollastonite nanowires. The obtained wollastonite nanowires could be used in fabrication of high strength calcium silicate bioceramics or bioactive nanocomposite with improved mechanical properties.

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References

1 M. Vukovich, *J. Am. Ceram. Soc.*, **39**, 323 (1956).
2 S. Hayashi, N. Otsuka, K. Akiyama, K. Okada, and T. Yano, *J. Ceram. Soc. Jpn.*, **97**, 742 (1989).
3 P. N. De Aza, F. Guitian, and S. De Aza, *Biomaterials*, **21**, 1735 (2000).
4 X. Y. Liu, C. X. Ding, and Z. Y. Wang, *Biomaterials*, **22**, 2007 (2001).
5 X. Y. Liu, C. X. Ding, and P. K. Chou, *Biomaterials*, **25**, 1755 (2004).
6 M. Risbud, D. N. Saheb, J. Jog, and R. Bhonde, *Biomaterials*, **22**, 1591 (2001).
7 L. Zhao and J. Chang, *J. Mater. Sci.: Mater. Med.*, **15**, 625 (2004).
8 P. Siriphannon, S. Hayashi, A. Yasumori, and K. Okada, *J. Mater. Res.*, **14**, 529 (1999).
9 K. L. Lin, J. Chang, Y. Zeng, and W. J. Qian, *Mater. Lett.*, **58**, 2109 (2004).
10 K. Yanagisawa, Q. Feng, and N. Yamasaki, *J. Mater. Sci. Lett.*, **16**, 889 (1997).
11 K. Kunugida, K. Tsukiyama, S. Teramura, S. Yuda, N. Isu, T. Shoji, and H. Takahashi, *Gypsum Lime*, **216**, 288 (1998).
12 K. Kubo, K. Mizuno, G. Yamaguchi, and H. Hayashi, *J. Ceram. Soc. Jpn.*, **82**, 45 (1974).
13 F. C. Meldrum, N. A. Kotov, and J. H. Fendler, *J. Phys. Chem.*, **98**, 4506 (1994).
14 M. Delsannti, A. Moussaid, and J. P. Munch, *J. Colloid Interface Sci.*, **157**, 285 (1993).
15 S. H. Han, W. G. Hou, W. X. Dang, J. Xu, J. F. Hu, and D. Q. Li, *Mater. Lett.*, **57**, 4520 (2003).
16 J. Yao, W. Tjandra, Y. Z. Chen, K. C. Tam, J. Ma, and V. Soh, *J. Mater. Chem.*, **13**, 3053 (2003).
17 Y. J. Xiong, Y. Xie, J. Yang, R. Zhong, C. Z. Wu, and G. A. Du, *J. Mater. Chem.*, **12**, 3712 (2002).