An Easy Method to Prepare Nanowire

Li Wang and Yongfa Zhu

Department of Chemistry, Tsinghua University, Beijng, 100084, P. R. China

$SrCO_3$ nanowires and $BaCO_3$ nanowires with single crystal structure and aspect ratio of about 1000 were prepared by a simple reaction without template. Preferentially assembling-reconstruction of colloidal particles was supposed as the formation mechanism.

Nanowires are of fundamental importance to the study of size- and dimensionality-dependent chemical and physical phenomena,[1–5] but how to rationally synthesize one-dimensional nanostructure materials is still a major challenge. Porous materials[6–8] and carbon nanotubes[9] are generally used as hard templates and surfactant micelles are usually used as soft templates[10–13] to synthesize nano-wires.

Here report an easy method to prepare $SrCO_3$ and $BaCO_3$ nanowire by a simple reaction. It will pioneer a new field in the synthesis of carbonate nanowires and related materials using assembling of colloidal particles. On the basis of the decomposition of carbonates, this new method can be extended to synthesize other nanowire materials such as salt, oxide and metal. Besides, on the basis of the unique performance of $SrCO_3$ and $BaCO_3$ material in low-temperature catalytic oxidation of VOC (volatile organic compound) and chemiluminescence sensor,[14] the related study on $SrCO_3$ nanowires was performed. The results reveal that $SrCO_3$ nanowires show lower catalyzing temperature, higher stability, higher activity and longer life, indicating its importance in development of low-temperature combustion catalyst and chemiluminescence sensors.
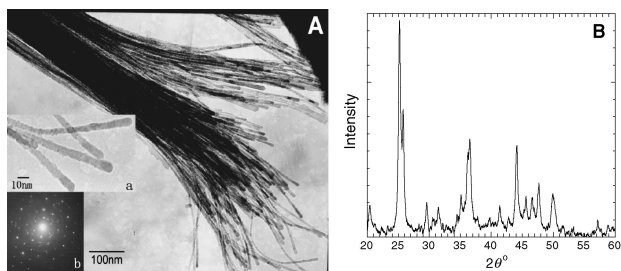

Figure 1. Characterization of typical $SrCO_3$ nanowires A: TEM micrograph along with the electron diffraction pattern; B: XRD patterns of $SrCO_3$ nanowires.

$SrCO_3$ nanowires were obtained by exposing fresh saturated $Sr(OH)_2$ solution to air, based on $Sr(OH)_2 + CO_2 \rightarrow SrCO_3\downarrow + H_2O$ reaction. A typical $SrCO_3$ nanowire sample, which was prepared by exposing fresh $Sr(OH)_2$ solution to air for 0.5 hour then being dried at $60\,°C$ for 16 h, was shown in Figure 1. Figure 1A showed the TEM micrograph with electron diffraction pattern and a magnified part of the sample. TEM photo indicated that most of $SrCO_3$ nanowires aggregated as regular bundles. The magnified part and electron diffraction pattern showed that the nanowires had uniform diameters of about 10 nm and was single crystal. The aspect ratios of $SrCO_3$ nanowires reached more than 1000 (average length of 10 μm and diameter of 10 nm).
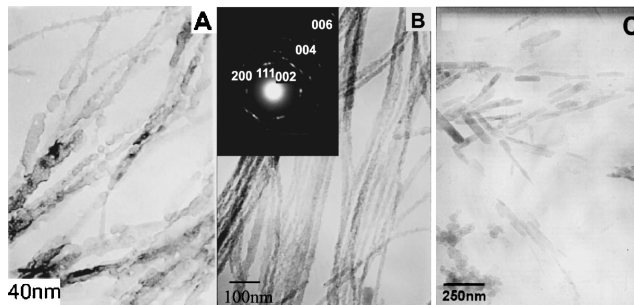

Figure 2. Effect of condition on nanowire growth A: react for 10 min; B: react for 60 min without heating; C: react with lower pH value.

Further characterization on composition and structure of the nanowires was performed using EDX (energy disperse X-ray analysis), LRS (laser Raman spectroscopy) and XRD (X-ray diffraction). EDX results indicated nanowires were consisted of strontic species, and LRS spectrum of the nanowires was the same with standard $SrCO_3$ powder. The XRD patterns of nanowire sample, as shown in Figure 1B, indicated that these peaks are attributed to the pure strontianite-type crystal according to the XRD standard spectrum of $SrCO_3$ powder.

The effects of time, temperature and pH on the growth of $SrCO_3$ nanowires were investigated systemically. As shown in Figure 2A, the nanowires showed a particle-particle-like discontinuous morphology when the reaction time was only 10 min, indicating nanowires were formed by assembling of particles. The particles were most ellipsoid with the long axis along the nanowires, indicating that the growth and assembling of colloidal particles were in certain direction.

Prolonging reaction time to 60 min at room temperature, the nanowires were apparently continuous and coarse, as shown in Figure 2B. The corresponding electron diffraction pattern of a nanowires bundle revealed a typical diffraction pattern due to a preferentially oriented fibrous texture. The diffraction pattern identified that the $SrCO_3$ nanowires are crystals of orthorhombic structure and only (00*l*) spots can be observed along the fiber axis, indicating that each wire is a single crystal with a preferential growth direction along the *c* axis.

The pH value of $Sr(OH)_2$ solution also has great influence on the formation of nanowires. Compared with the typical $SrCO_3$ nanowire sample, the aspect ratio of nanowire decreased dramatically from 1000 to 4 with pH value of solution decreasing from 14 to 12, as seen in Figure 2C. This revealed the role of OH^- in adsorb predacious growth and assembling process.

On the basis of above results, a formation mechanism of SrCO$_3$ nanowires was supposed as a directional assembling-reconstruction of colloidal particles. Firstly, some Sr(OH)$_2$ reacted with CO$_2$ to form SrCO$_3$ colloidal particles, and OH$^-$ anion intended to be adsorbed on the crystal faces parallelling to the c axis of the primary nuclei, resulting in the anisometric primary SrCO$_3$ colloidal particles. Then, the colloidal particles assembled in a certain direction through their c axes to form the particle-particle-like nanowires. The particle-particle-like nanowires tended to recombine in solution, and continuous nanowires formed as a consequence. Nanowires grew to perfect single crystalline when appropriate reconstruction condition was provided, such as suitable temperature and time.

Since no template was used in the preparation nanowires, the preferential growth of SrCO$_3$ crystal can be attributed to the high chemical potential along c axis. On the basis of the influence of chemical potential on the shape evolution of nanocrystal elucidated by Peng et al., in the case of one-dimensional nano-structure growth it would be advantageous to have a higher chemical potential,[15,16] which is mainly determined by the pH value in our work as shown in Figure 2C.

BaCO$_3$ nanowires prepared by the same method showed the similar morphology, length and diameter with SrCO$_3$ nanowires, as shown in Figure 3. This revealed the potential application of this method in preparation of other nanowire materials.

The SrCO$_3$ nanowire showed good catalytic performance for catalytic oxidation of formaldehyde. Its start and complete combustion temperature was 80 °C and 100 °C lower than that of SrCO$_3$ nanoparticle when the initial concentration was 800 ppm. Its complete combustion temperature was 140 °C lower than that of SrCO$_3$ nanoparticle at high concentration (7000 ppm) and it did not lost activity, indicating its great advantages in the catalytic oxidation of VOC. Besides, its catalytic luminescence based on catalytic oxidation of ethanol[14] was intensified linearly with temperature below 360 °C and kept constant at higher temperature, indicating the advantages in the performance as chemical luminescence sensor.

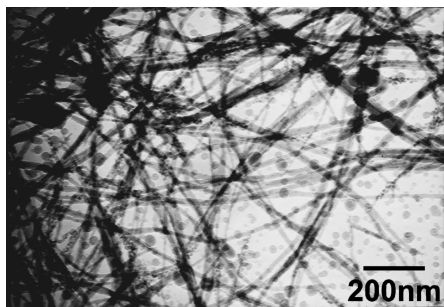**Figure 3.** As-prepared BaCO$_3$ nanowire.

References and Notes

1 R. M. Dickson and L. A. Lyon, *J. Phys. Chem. B*, **104**, 6095 (2000).
2 Y. M. Lin, S. B. Cronin, J. Y. Ying, M. S. Dresselhaus, and J. P. Heremans, *Appl. Phys. Lett.*, **76**, 3944 (2000).
3 R. Dagani, *Chem. Eng. News*, **79**, 14 (2001).
4 J. F. Wang, M. S. Gudiksen, X. F. Duan, Y. Cui, and C. M. Lieber, *Science*, **293**, 1455 (2001).
5 M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science*, **292**, 1897 (2001).
6 M. H. Huang, A. Choudrey, and P. D. Yang, *Chem. Commun.*, **12**, 1063 (2000).
7 C. R. Martin, *Science*, **266**, 1961 (1994).
8 C. Huber, M. Sadoqi, T. Huber, and D. Chacko, *Adv. Mater.*, **7**, 316 (1995).
9 L. M. Cao, Z. Zhang, and L. L. Sun, *Adv. Mater.*, **13**, 1701 (2001).
10 D. B. Zhang, L. M. Qi, J. M. Ma, and H. M. Cheng, *Chem. Mater.*, **13**, 2753 (2001).
11 L. M. Huang, H. T. Wang, Z. B. Wang, A. Mitra, K. N. Bozhilov, and Y. S. Yan, *Adv. Mater.*, **14**, 61 (2002).
12 B. H. Hong, S. C. Bae, C. W. Lee, S. Jeong, and K. S. Kim, *Science*, **294**, 348 (2001).
13 D. B. Zhang, L. M. Qi, J. M. Ma, and H. M. Cheng, *Chem. Mater.*, **13**, 2753 (2001).
14 J. J. Shi, J. J. Li, Y. F. Zhu, F. Wei, and X. R. Zhang, *Anal. Chim. Acta*, **466**, 69 (2002).
15 Z. A. Peng and X. G. Peng, *J. Am. Chem. Soc.*, **123**, 1389 (2001).
16 Z. A. Peng and X. G. Peng, *J. Am. Chem. Soc.*, **124**, 3343 (2002).
17 Since hydrolyzing of SrAl$_2$O$_4$ can be easily controlled, it was used as source of fresh Sr(OH)$_2$ solution. After SrAl$_2$O$_4$ powder dispersed in distilled water by ultrasonic bath for 10 min, the by-produced Al(OH)$_3$ was removed by centrifugation. Then Sr(OH)$_2$ exposed to air at deferent temperature for desired time. Finally, the product was washed with 10% NaOH solution and distilled water by turn to removed the residual Al(OH)$_3$. The TEM analysis was obtained in a Hitachi H-800 system, with accelerating voltage for electron beam of 200 kV. The preparation of sample for LRS analysis was the same as that for TEM, except for the substrate was glass. LRS was carried out on Renishaw 2000 system. XRD experiments were carried out using a Rigaku DMAX-2400 diffractometer with Cu Kα radiation. Characterization of electron diffraction is based on $R = K/d$ (R is the distance between spot and (000), K is camera constant and d is the distance between crystal faces) and an important reference (*J. Phys. Chem. B*, **101**, 3460 (1997)). The important data were listed as following. Lttice constants $a = 5.10$ Å, $b = 8.40$ Å, $c = 6.02$ Å, and camera constant $K = 20.08$ mm·Å. The standard d from JCPDS (84-1778) was applied to calibrate the diffraction spots.