

Synthesis and Characterization of Strontium Carbonate Nanowires with *a* Axis Orientation and Dendritic Nanocrystals

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Strontium carbonate nanowires that grow along the *a* axis were synthesized in large scale through simple hydrothermal approach for the first time. The aspect ratio of the product is more than 1000. Dendritic nanocrystals were also generated at low temperatures. Moreover, this method is feasible to be applied in the synthesis of barium carbonate nanowires.

One-dimensional (1-D) nanostructures, such as nanotubes, nanowires, and nanorods are critically important to chemistry, optics, magnetics, and electronics, and hence have great promise for improving our understanding of fundamental concepts of both dimensionality and size on physical properties, as well as for application in nanodevices.¹ Therefore, extensive efforts have been made to synthesize these bulk 1-D nanostructure materials, especially nanowires. Many methods have been developed and reviewed elsewhere.² But up to the present, the advance in the taking advantage of nanowires has been relatively slow. The major problems seem to be the methods used, purity or crystallinity of the products and control of component.³ In order to resolve these synthetic challenges, many in-depth studies should be performed. Carbonate materials are crucial raw materials to synthesize other compounds. Moreover, they are also widely applied in the inorganic-organic hybrid composite materials as fillers. Hence, the morphology and size of carbonate are much more significant to determine the properties of hybrid composite materials.⁴ A few works have been reported to prepare barium carbonate nanowires through reverse micelles or microemulsions approach.⁵ However, to the best of our knowledge, the strontium carbonate nanowires have not been intensively studied.⁶ Herein, we introduce a novel simple hydrothermal method without surfactant to synthesis strontium carbonate nanowires with *a* axis orientation for the first time. The width of nanowires ranges from 20 to 200 nm and the length is more than 10 μ m. Dendritic nanostructure is also observed in the strontium carbonate. Moreover, this approach is also feasible for synthesis of barium carbonate nanowires.

The chemicals used are of analytical grade. Typically, 0.1 mmol strontium acetate ($\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, Shanghai Chemical Reagent Co., Ltd), 20 mmol NaOH and 0.4 mmol 2-aminoethanethiol (AET; $\text{HSCH}_2\text{CH}_2\text{NH}_2$, ACROS ORGANICS) were added into 30-mL distilled water. After stirring for 5 min, this solution was transferred into a 35-mL Teflon-lined stainless-steel autoclave and performed hydrothermal treatment at 120–180 °C for 12 h. Barium acetate instead of strontium acetate was used when synthesizing the barium carbonate while other conditions remain the same. The final products were filtered

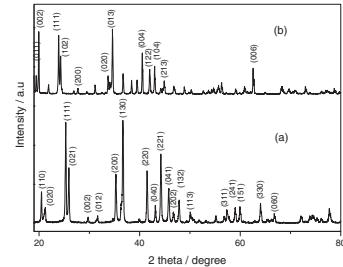


Figure 1. X-ray diffraction spectra of (a) strontium carbonate and (b) barium carbonate nanowires synthesized at 160 °C for 12 h.

out, washed with distilled water and ethanol in subsequence, and later dried in a vacuum oven at 60 °C for 12 h.

The products were characterized by using X-ray powder diffraction (XRD, D/max 2550 V) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). High-resolution transmission electron microscopy (HRTEM) images were taken on JEOL 4000 FX microscope equipped with double-tilt holder and operated at 400 kV. TEM (JEM-2010, 200 kV) with EDX attachment was also applied to observe the micromorphology.

The X-ray diffraction (XRD) spectra of strontium carbonate and barium carbonate synthesized at 160 °C can be indexed to orthorhombic phase (space group: $Pmcn$) according to JCPDS 05-0418 and 45-1471, respectively (Figure 1). It is worth noting that in the XRD spectrum of strontium carbonate the peak of (200) plane is obviously strengthened, which imply the anisotropic growth along identical orientation (Figure 1a).

Figure 2 visualizes the morphologies of products synthesized at different temperatures. The strontium carbonate nanowires were successfully synthesized at 160 °C for the duration

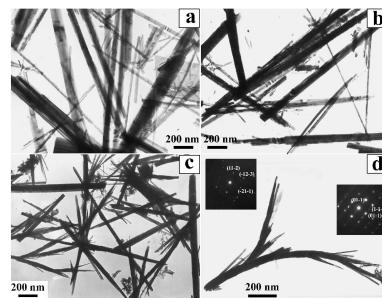


Figure 2. TEM images of strontium carbonate nanowires synthesized at (a) 160 °C for 12 h and (b) 180 °C for 12 h. The inset is SAED pattern of single nanowires. (c) Strontium carbonate dendritic nanostructure synthesized at 130 °C for 12 h. (d) Typical dendritic nanocrystal and the corresponding SAED pattern of different positions.

12 h (Figure 2a). The widths of nanowires range from 20 to 200 nm and the length is more than 10 μm . Aspect ratio of nanowires exceeding 1000 is dominant in our samples. Moreover, these nanowires are slightly transparent in the TEM images, which indicates the thickness of nanowires is less than the width (ratio of width and thickness is about 5). The nanowires are all straight and flat which shows the stiffness characteristic of nanowires and indicates the promising application in the inorganic-organic hybrid composites as a strengthening phase. This morphology of strontium carbonate is distinct from the previous report in which the nanowires are curved and assembled by some tiny particles.⁵ Figure 2b shows the TEM image of sample synthesized at 180 $^{\circ}\text{C}$. Comparing these two samples, the morphology and size of products have no obvious difference when the reaction temperature elevates. But at lower temperature (for example 130 $^{\circ}\text{C}$), dendritic nanocrystals other than nanowires formed as shown in Figure 2c. The width of trunk is 80 nm, and the branch's width is as small as 20 nm. Figure 2d is the typical morphology of strontianite dendritic crystal. SAED analysis shows the different orientations of trunk and branches (inset in Figure 2d), where trunk is along the [1-1-2] orientation and branches are along the [11-2] orientation.

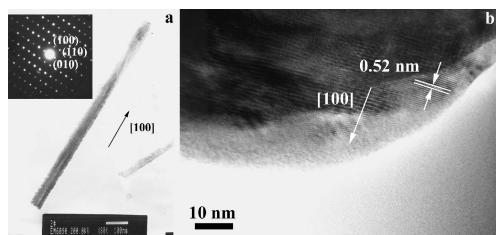


Figure 3. (a) TEM image of single strontium carbonate nanowire obtained at 160 $^{\circ}\text{C}$ for 12 h, inset is SAED pattern along [001] zone axis and (b) its corresponding HR-TEM image.

The strontianite nanowires' growth habit seems to be different from the dendritic nanostructure. The SAED pattern inserted in Figure 3a is taken along the [001] zone axis, which illustrates that the nanowires prefer to grow along the [100] orientation. This anisotropic growth is well consistent with the XRD result that peak of (200) plane largely enhanced when comparing with the standard XRD spectrum. High resolution TEM image is also presented here and clearly show that the (100) plane (interplanar spacing is 0.52 nm) is the preferential growth plane (Figure 3b). This orientation also is different from the strontium carbonate reported whose preferential orientation is along *c* axis.⁵

The formation of carbonate process is proposed by following equations that are often used to fabricate methane gas:



Using this simple method, the barium carbonate nanowires can also be synthesized. TEM image illustrates ultra-long nanowires as same as strontium carbonate nanowires were obtained. The average width is about 320 nm and length is mostly longer than 10 μm . SAED analysis indicates the nanowires preferentially grow along the [001] orientation, which is consistent with the previous reports.^{6b,6d} HR-TEM image taken at the tip of nanowire further confirms the anisotropic growth (Figure 4b). The crystal plane (001) whose lattice spacing is 0.63 nm is perpendicular to the growth direction. In the XRD spectrum (Figure 1b),

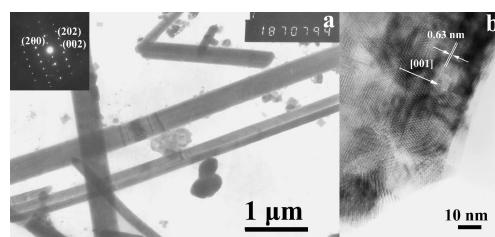


Figure 4. TEM image of barium carbonate nanowires, inset is SAED pattern along [010] zone axis and (b) its corresponding HR-TEM image.

peaks including (002), (004), and (006) are dramatically strengthened, which corroborate the SAED and HRTEM results.

The exact growth mechanism of the nanowires is not fully understood. We think the AET molecules added should play an important role. Control experiments were performed with no AET molecules while maintaining other condition. The resultant strontium carbonate or barium carbonate is irregular agglomerates rather than nanowires (not show here). The thiol and amine groups in the organic molecule are always used to bind metal cation to form complexes. Thus, directed adsorption of AET molecules on the specified planes is reasonably proposed to account for the anisotropic growth phenomena. Morphology evolution from dendritic nanostructure to nanowire also should be due to the different adsorption ability on different planes at varied temperatures that results in the change in the growth rate of different planes. It is interesting that the strontium carbonate nanowires grow along *a* axis instead of *c* axis which was the preferential orientation of barium carbonate nanowires although these two materials have the same crystal structure. In order to explore in depth the formation mechanism of carbonate nanowires and dendritic nanostructures, further studies are now in progress in our laboratory.

In conclusion, we herein introduce a novel method to synthesize the high aspect ratio (more than 1000) strontium carbonate nanowires with *a* axis orientation. Dendritic nanostructures were also controllably formed at low temperatures. Moreover, this method is feasible to be applied in the synthesis of barium carbonate nanowires. The formation mechanism of resultant morphology is proposed by directed adsorption of AET molecule on specific crystal planes.

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