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Controlled synthesis of $SrCO_3$ dendrites by a simple hydrothermal method

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In this paper, we report the controlled synthesis of $SrCO_3$ crystals by a simple hydrothermal method without any surfactants and templates. The as-prepared samples were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The effect of pH value, temperature, and reaction time on the formation of $SrCO_3$ crystals was investigated. This novel route is proved to be simple and environment-friendly, which can be extended to the shape-controlled synthesis of other metal oxide nanocrystals.

Key words: $SrCO_3$ dendrites, Controlled synthesis, a simple hydrothermal method.

Introduction

Recently, strontium carbonate ($SrCO_3$) has attracted considerable research interest due to its wide applications in many industrial fields, including special glass, electronics, catalyst, ceramics, papers, pigment, pyrotechnics, chemical industry and so on [1-3]. It is well known that the properties of nanocrystals are greatly dependent on the morphology and grain size [4]. So far, a variety of $SrCO_3$ crystals with different morphologies have been successfully obtained. $SrCO_3$ microrods, hexahedral ellipsoids, and hexagonal pyramid have been synthesized by the solvothermal/ hydrothermal route [5-7]. $SrCO_3$ crystals with olive-, flowers-, rod-, spindle- and star-like morphologies have been prepared by the assistance of organic solvents [8-11]. Especially, $SrCO_3$ dendrites have been fabricated by the assistance of ethylenediamine [12]. However, these methods involved the use of large amounts of toxic organic agents, and the processes were complex and limited. Now, it is still a significant challenge for material researchers to control the shape of $SrCO_3$ crystals by a simple process, which would be of great importance for broadening and improving their industrial applications.

In our previous work, we have successfully synthesized $PbTiO_3$ nanowires via the hydrothermal method [13]. In this paper, we first report the morphology-controlled synthesis of $SrCO_3$ dendrites by a simple hydrothermal method without any templates or surfactants. This green chemistry method is simple and highly reproducible, which can be extended to the shape-controlled synthesis of other metal oxide nanocrystals. To the best of our knowledge, no such study has ever been reported.

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Experimental

All the chemicals were analytical grade purity. In a typical experiment, K_2CO_3 and $Sr(NO_3)_2$ were used as the starting materials. Firstly, equimolar amounts K_2CO_3 and $Sr(NO_3)_2$ were separately dissolved in distilled water to form aqueous solutions. Then, the $Sr(NO_3)_2$ solution was slowly added to K_2CO_3 solution by constant stirring. Finally, the mixed precipitate solution was transferred into a 50 ml stainless-steel autoclave for a hydrothermal treatment. The autoclave was sealed, heated to 120 °C and held for 2 hrs, and then cooled to room temperature naturally. The resultant precipitates were centrifuged, washed with distilled water, and dried naturally for characterization. The effect of precursor, temperature, and pH value on the formation of $SrCO_3$ was investigated. The pH value of the mixed solution in the autoclave was adjusted to 7 and 14, respectively.

X-ray diffraction was performed on an X-ray diffractometer (D8 Focus, Germany) using CuKα radiation. Transmission electron microscope (TEM, JEM-2100, Jeol, Japan) images were taken with an acceleration voltage of 200 kV.

Results and Discussion

The effect of pH value and reaction temperature on the formation of $SrCO_3$ nanocrystals was studied. Figs. 1(a-b) displays the XRD patterns of the as-prepared samples prepared by the hydrothermal process at 120 °C with different pH values. It is found that all the diffraction peaks could be indexed to a pure phase $SrCO_3$ with an orthorhombic structure, well consistent with the literature data (JCPDS: 84-1778). Furthermore, different pH values did not bring about significant changes in the XRD patterns, implying that the variation

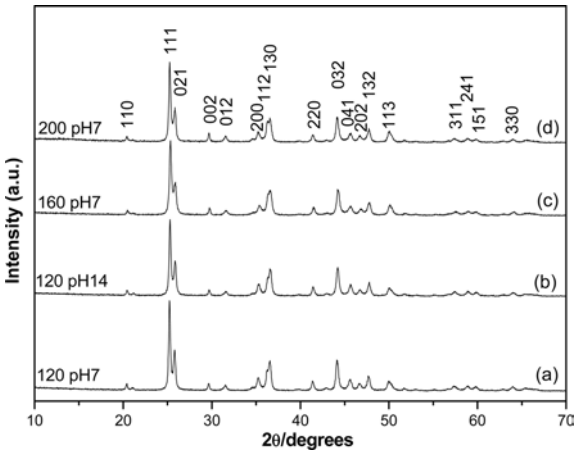

Fig. 1. Powder X-Ray diffraction patterns of the as-prepared $SrCO_3$ samples prepared by the hydrothermal process at different reaction temperatures and pH values: (a) 120 °C and pH7, (b) 120 °C and pH14, (c) 160 °C and pH7, (d) 200 °C and pH7.

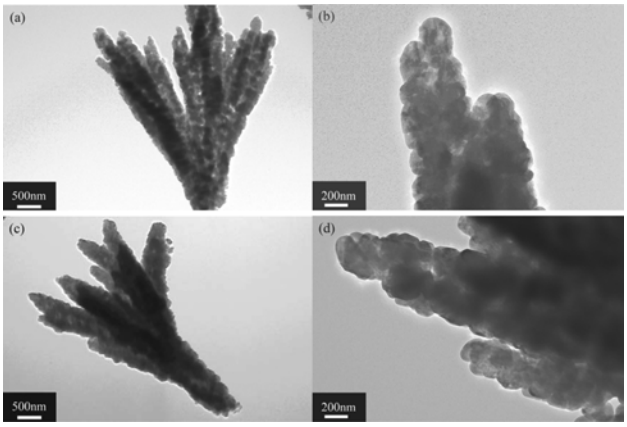

Fig. 2. TEM images of the as-prepared $SrCO_3$ samples prepared by the hydrothermal process at 120 °C with different pH values: (a) 7 and (c) 14, respectively. (b,d) higher magnication TEM image of the obtained $SrCO_3$ dendrites.

of pH values bring a weak influence on the formation of $SrCO_3$ nanocrystals. When the reaction temperature was increased from 120 °C to 160 °C and 200 °C (Figs. 1(c-d)) at pH7, it is clear that the XRD patterns are almost similar and all the diffraction peaks can be indexed to a pure phase $SrCO_3$ with an orthorhombic structure. The sharp diffraction peaks indicate that well crystallized $SrCO_3$ nanocrystals can be prepared under the current synthetic conditions.

Fig. 2 illustrates the TEM images of the as-prepared $SrCO_3$ samples synthesized by the hydrothermal method at 120 °C with different pH values. As displayed in Fig. 2(a) and Fig. 2(c), it is interesting to observe that the obtained $SrCO_3$ samples were well-defined dendrites. The diameter and length of the branches are about 200-300 nm and 2-3 μm, respectively. Higher magnification TEM images of the $SrCO_3$ dendrites are presented in Figs. 2(b, d), which clearly reveals that the dendritic microstructure was formed by the self-assembly of nanoparticles with diameters of 150-200 nm. When the

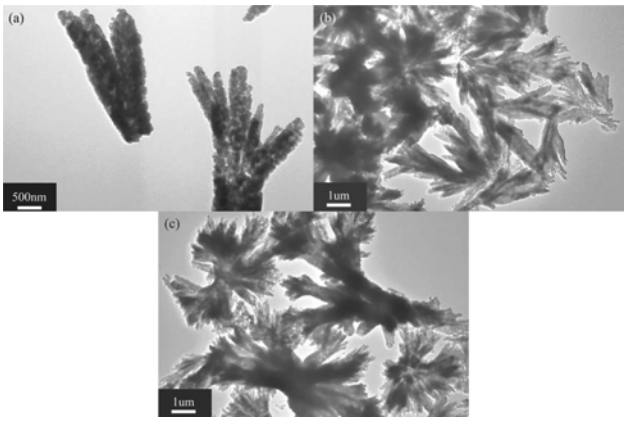

Fig. 3. TEM images of the as-prepared $SrCO_3$ samples prepared by the hydrothermal process at pH7 and different temperatures: (a) 120 °C, (b) 160 °C, and (c) 200 °C, respectively.

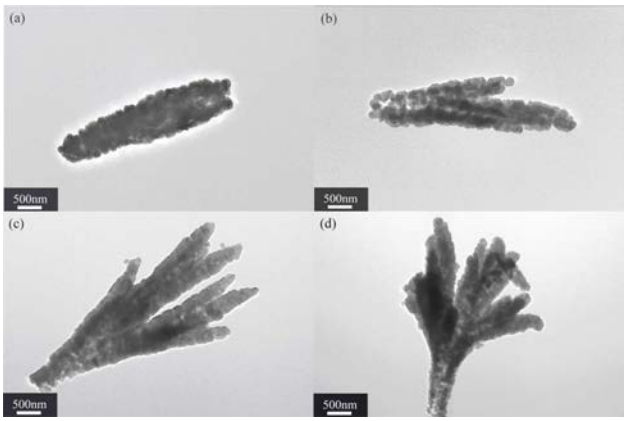

Fig. 4. TEM images of the as-prepared $SrCO_3$ samples prepared by the hydrothermal process at pH7 and 120 °C for (a) 10 min, (b) 30 min, and (c) 1 hr, and (d) 2 hrs, respectively.

reaction temperature was increased from 120 °C to 160 °C and 200 °C, as depicted in Fig. 3, $SrCO_3$ crystals with a dendritic structure were obtained, which indicated that well crystallized $SrCO_3$ dendrites can be successfully synthesized by the hydrothermal process.

A detailed time course study is expected to provide direct evidence of the $SrCO_3$ dendrites formation process. Fig. 4 illustrates the TEM images of the as-prepared $SrCO_3$ samples obtained during the reaction course. As depicted in Fig. 4(a), $SrCO_3$ trunks were first formed in the case of 10 min. When the reaction time was increased from 10 min to 30 min, as displayed in Fig. 4(b), branches began to emerge. As the reaction time was further increased to 1 h and 2 hrs, as shown in Figs.4(c-d), $SrCO_3$ dendrites with more branches were finally formed. From Figs. 4(a-d), one can clearly see the formation process of $SrCO_3$ dendrites assembled from nanoparticles.

$SrCO_3$ branch-like crystals have been successfully prepared by a microwave-assisted aqueoussolution method [12], which must be assisted by the organic additives. However, no surfactants or templates are introduced into the present reaction system. Therefore, we consider

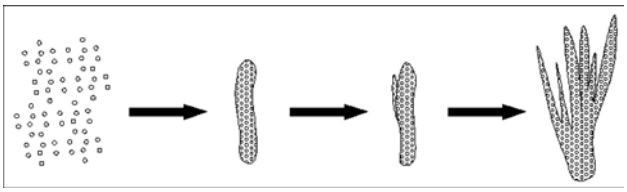

Fig. 5. Schematic illustration of the growth of $SrCO_3$ dendrites.

that the reduction of surface energy should be the primary driving force for the $SrCO_3$ crystal growth in this experiment. The formation process of $SrCO_3$ crystals is depicted schematically in Fig. 5. As the reaction mechanism and hydrothermal conditions are complicated, the exact mechanism for the controllable synthesis of $SrCO_3$ crystals still needs to be further investigated.

Conclusions

In summary, we have developed a simple hydrothermal method to the controlled synthesis of $SrCO_3$ dendrites without any surfactants and templates. Moreover, this novel route is proved to be simple and environment-friendly, which may be extended to the shape-controlled synthesis of other metal oxide nanocrystals.

Acknowledgments

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