

Preparation of Elongated Hexagonal Pyramids and Hexagonal Prisms of SrCO₃ Using Hydrothermal Reactions

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Strontium carbonate (SrCO₃) is important inorganic material and is widely used as an additive in the glass of color television tubes to block X-rays and improve glass quality. SrCO₃ is also used in ferrite magnets, pigments, iridescent materials, and as a catalyst.¹⁻³ The development of specific microstructure morphologies has attracted significant interest due to their novel properties and potential applications.^{4,5} Recently, a variety of SrCO₃ micro- and nano-structures, such as rods, wires, ribbons, flowers, hexagonal prisms, and spheres, have been synthesized.⁶⁻⁹ Furthermore, soft-templates are commonly used to fabricate SrCO₃ crystals with specific morphologies. For example, dumbbell-like crystals were prepared using a poly(styrene-*alt*-maleic acid), and ribbon- and flower-like crystals were prepared using anionic surfactant and mixed nonionic/anionic surfactants, respectively.¹⁰⁻¹² In this paper, we report a simple hydrothermal method free of surfactants that can be used to prepare elongated hexagonal pyramidal SrCO₃ crystals from strontium nitrate and urea. Furthermore, the aspect ratios of the hexagonal prisms and rods produced were controlled by adding *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the hydrothermal reaction between Sr(NO₃)₂ and urea as a structure-directing agent.

Experimental Section

Sr(NO₃)₂ (99%, Aldrich), Na₂CO₃ (99.5%, Aldrich), urea (98%, Aldrich), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 98%, TCI) were used as received. SrCO₃ was prepared in three ways. 1) For the precipitation method, 10 mL of 0.1 M Sr(NO₃)₂ aqueous solution was added to 10 mL of 0.1 M Na₂CO₃ aqueous solution, stirred for 1 min, and allowed to stand at room temperature for 30 min. 2) For the hydrothermal method, 50 mL of 0.1 M Sr(NO₃)₂ was added to 50 mL of 0.1 M urea and stirred for 1 min. A 70 mL aliquot of this solution was then transferred to a 100 mL Teflon-lined autoclave and heated at 90 °C for 16 h. 3) For the ligand-assisted hydrothermal method, different concentrations of TMEDA from 0.1 M to 1.6 M were added to the 0.1 M Sr(NO₃)₂ solution and then 0.1 M urea was added. A 70 mL aliquot this mixed solution was then transferred to a 100 mL capacity Teflon-lined autoclave and heated at 90 °C for 16 h. All products obtained using the three different methods were filtered, washed several times with water and ethanol, and then dried at 60 °C for 24 h.

The structures of the SrCO₃ products so obtained were analyzed by powder X-ray diffraction (XRD, PANalytical,

X'pert PRO MPD) using Cu K α radiation, and their morphologies were determined by scanning electron microscopy (SEM, Hitachi S-4300).

Results and Discussion

Figure 1 shows an SEM image of SrCO₃ prepared by simple precipitation. The product was composed of rod-like microparticles of average length 7 μ m. Figure 1(B) shows the rod-like particular aggregates formed, from small particles of average size 500 nm. Accordingly, simple precipitation resulted in the formation poor microcrystal morphologies, which had a rod-

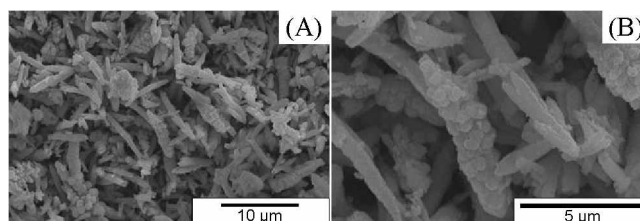


Figure 1. SEM images of SrCO₃ obtained using simple precipitation from 0.1 M Sr(NO₃)₂ and 0.1 M Na₂CO₃ at room temperature.

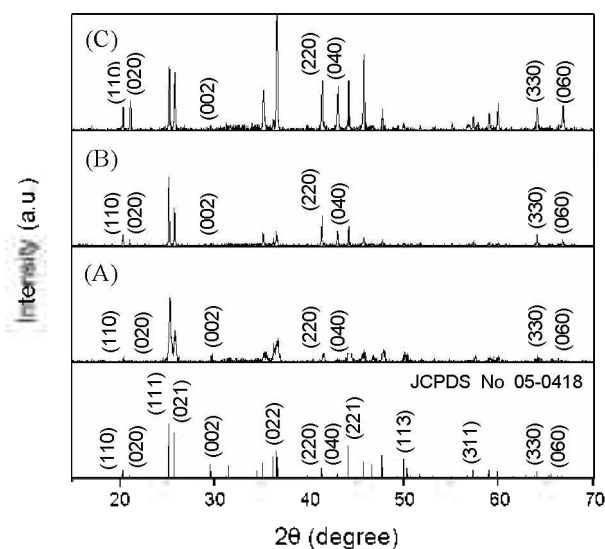


Figure 2. X-ray diffraction patterns of SrCO₃ products obtained using (A) simple precipitation, (B) the hydrothermal method, and (C) the ligand-assisted hydrothermal method.

like appearance (Figure 1(B)). Figure 2(A) shows the XRD pattern of this product. All peaks were assigned to the orthorhombic phase of SrCO_3 and coincided with literature values (JCPDS 05-0418, $a = 5.107 \text{ \AA}$, $b = 8.414 \text{ \AA}$, $c = 6.029 \text{ \AA}$). Since no other peaks were detected, it indicates that this method yields SrCO_3 free from impurities.

Figure 3 shows an SEM image of the SrCO_3 prepared using the hydrothermal method between $\text{Sr}(\text{NO}_3)_2$ and urea in water at 90°C for 16 h. Urea decomposes at temperatures above 80°C in aqueous solution to release CO_3^{2-} ions.¹³ The SrCO_3 particles prepared using the hydrothermal method had an elongated hexagonal pyramidal morphology (Figure 3(A)) with an average base width of $\sim 6.5 \mu\text{m}$ and a length of $40 \mu\text{m}$ (an aspect ratio is ~ 6). Figure 3(B) shows the tips area of these elongated SrCO_3 microcrystals, which were found to grow along the c -axis. The front three side faces shown in Figure 3(B) were indexed as $(\bar{1}10)$, (010) , and (110) planes, and the six end-capped faces as $(\bar{1}11)$, (011) , (111) , $(\bar{1}\bar{1}1)$, $(0\bar{1}1)$, and $(1\bar{1}1)$ planes. Figure 2(B) shows the XRD patterns of this product. A comparison with the relative intensities shown in Figure 2(A) indicates that the two products were obviously different. The relative intensities of (110) , (020) , (220) , (040) , (330) , and (060) of Miller indices in Figure 2(B) are higher than those in Figure 2(A), but that of (002) is lower, which indicates that in the hydrothermal reaction product the elongated hexagonal pyramidal axes of the SrCO_3 microcrystals were aligned along the orthorhombic crystallographic c -axis, namely, in the $[001]$ direction.

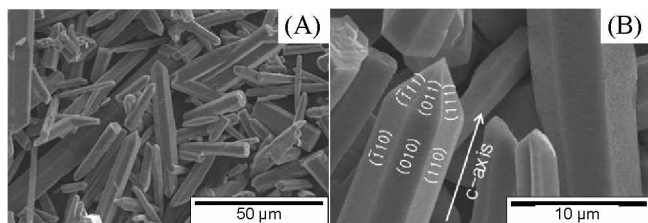


Figure 3. SEM images of SrCO_3 microcrystals prepared using the hydrothermal method.

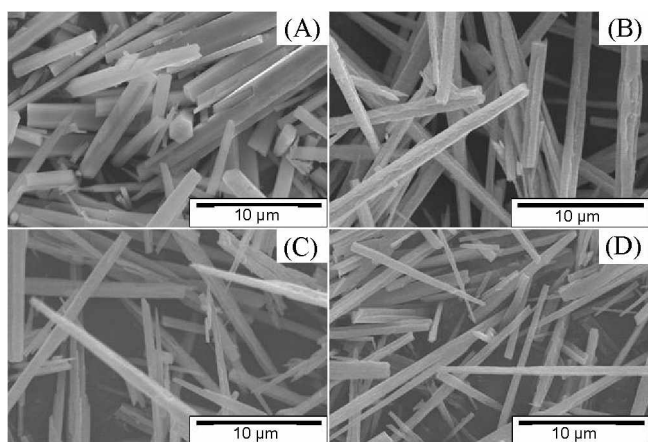
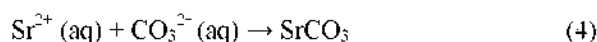
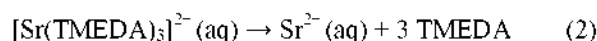
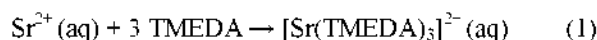


Figure 4. SEM images of the SrCO_3 substantially prepared using the ligand-assisted hydrothermal method from $\text{Sr}(\text{NO}_3)_2$ with urea in aqueous solution at 90°C for 16 h in the presence of different concentrations of TMEDA; (A) 0.1 M, (B) 0.4 M, (C) 0.8 M, and (D) 1.6 M.

Figure 4 shows SEM image of a product prepared using the ligand-assisted hydrothermal method, which involved the use of different concentrations of TMEDA. In terms of morphologies the SrCO_3 product obtained appeared as a mixture of hexagonal prisms and rods. When the concentration of TMEDA was increased from 0.1 M to 1.6 M, while keeping the concentrations of $\text{Sr}(\text{NO}_3)_2$ and urea constant, the aspect ratios of the microcrystals obtained increased ~ 7 to ~ 18 . Moreover, the number of microcrystals with a rod-like morphology increased on increasing TMEDA concentration. Figure 2(C) shows the XRD pattern of the ligand-assisted product. The relative intensities of the (110) , (020) , (220) , (040) , (330) , and (060) of Miller indices in Fig. 2(C) are higher than those in Figure 2(A) and 2(B). Accordingly, TMEDA was found to act as a morphology modifying agent.

In terms of the ligand-assisted hydrothermal method, TMEDA was used to strongly chelate Sr^{2+} to form the stable $[\text{Sr}(\text{TMEDA})_3]^{2+}$ complex. TMEDA is a stronger chelator than ethylenediamine, because of the electron donating effect that four methyl groups have on the two nitrogen atoms. Furthermore, this chelating effect of TMEDA is evidently strong enough under the conditions used to reduce substantially the availability of Sr^{2+} ions. Thus, we attribute the particle morphology modifying effect of TMEDA to the limited availability of Sr^{2+} and the stability of the TMEDA complexes formed.

The set of ligand-assisted hydrothermal reactions involved in the formation of SrCO_3 for are as follows:



In general, the heavy metal carbonates (MCO_3 , $\text{M} = \text{Sr}$, Ba , or Pb) form crystals in $Pm\bar{c}n$ crystallographic space group that consist of layers of nine-coordinated metal atoms in a hexagonal closest packed structure.¹³ Therefore, it appears that SrCO_3 has a unique hexagonal prismatic morphology in which the long axis perpendicular to the hexagonal plane. When SrCO_3 was prepared using the precipitation method, the rapidly formed SrCO_3 microparticles were non-crystal like and subsequently aggregated to form rods. In the hydrothermal method carbonate ions were slowly released by the decomposition of urea, and the SrCO_3 formed had sufficient time to produce elongated hexagonal pyramidal microcrystals. On the other hand, the TMEDA formed a stable complex with strontium, and both carbonate and strontium ions were released very slowly, and thus, varying TMEDA concentrations modulated particle morphology.

In conclusion, SrCO_3 crystals with various morphologies were prepared using precipitation and two hydrothermal methods. SrCO_3 rod-like microparticles were prepared by simple precipitation from strontium nitrate with sodium carbonate in aqueous solution. On the other hand, SrCO_3 elongated hexagonal pyramidal microcrystals were synthesized using a hydro-

thermal method by reacting strontium nitrate and urea in aqueous medium. In addition, SrCO₃ hexagonal prism and rod microcrystals were also prepared using a ligand-assisted hydrothermal method between strontium nitrate, urea, and the metal chelating agent *N,N,N',N'*-tetramethylethylenediamine (TMEDA). During this latter preparation as the concentration of TMEDA was increased, SrCO₃ microcrystal shapes changed from hexagonal prisms to hexagonal rods with high aspect ratios. XRD results showed that these elongated hexagonal pyramids and hexagonal prisms resulted from growth along the crystallographic orthorhombic *c*-axis.

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