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Morphology of Strontium Carbonate Particle Adjusted by Phthalic Acid and Isophthalic Acid

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Abstract. $SrCO_3$ crystals with various morphologies were prepared using precipitation method by the reaction of Na_2CO_3 and $SrCl_2$ in aqueous solution in the presence of isophthalic acid and phthalic acid, respectively, which were used as crystal growth adjusters. When isophthalic acid was used as the adjuster, the major morphologies of $SrCO_3$ were center-bundled and two ends emission growing clusters formed by the self-assembling of short rod whiskers. While using phthalic acid as the adjuster, flower-like $SrCO_3$ clusters were assembled by needle-shaped whiskers when the concentration was low. But the morphologies changed from flower shape to sphere shape with the increasing amount of phthalic acid. The results indicate that the morphology of $SrCO_3$ may be adjusted by the structure of carboxylic acid.

1. Introduction

The development of specific microstructure morphologies and controllable morphosynthesis of inorganic materials with specific size, shape and phase etc. by using diverse synthetic methods has attracted research interest, because shape control and structural speciality have significant effects for the properties in various fields [1,2]. Aragonite-type $SrCO_3$, strontianite, is widely used as an additive in the glass of color television tubes to block X-rays and improve glass quality. $SrCO_3$ is also used in ferrite magnets, pigments, iridescent materials, pyrotechnics, a precursor for various strontium compounds, and as a catalyst [3-6]. Therefore, $SrCO_3$ is a very important inorganic material and the development of specific microstructure morphologies has attracted more and more attention because of their novel properties and potential applications [7,8]. Many methods for the fabrication of $SrCO_3$ (micro/nanostructures) have been reported, including refluxing process [9], catalytic decomposition [10], self-assembled monolayers [11], hydrothermal method [12,13], microemulsion mediated solvothermal method [14], homogeneous precipitation by enzyme-catalyzed reaction [10], biological synthesis using the fungus fusarium oxysporum [15] and so on. Strontianite with different morphologies such as spheres and ellipsoids [14,16], olive-like and flower-like nanostructures [17,18], and 1D nanostructures have been synthesized [15,19]. In addition, a variety of $SrCO_3$ rods, wires, ribbons, hexagonal prisms et al. micro- and nano-structures have been synthesized [20-22]. The effects of the concentration of PSMA(poly-(styrene-alt-maleic acid)) on the morphologies and phase structures of strontium carbonate particles were investigated by Yu et al. The results showed that $SrCO_3$ particles with various shapes, for example, bundles, dumbbells, irregular aggregates and spheres could be obtained by varying the concentration of PSMA [23]. Huang et al. synthesized and reported $SrCO_3$ in the presence of nonionic/anionic surfactants F127/SDS in the water or alcohol. $SrCO_3$ particles change from pancakes to flowers, and then to irregular flakes [24].

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It is well known that phthalic acid (PA) and isophthalic acid (IPA) can coordinate with Sr(II) ion and therefore, may control the initial growth and further assemblies of $SrCO_3$ particles, at micro- and nanoscale level, into target structured materials bearing the controlled size and tailored morphology [25]. Therefore, in this work, we reported a facile and direct method for hierarchical $SrCO_3$ in presence of appropriate amount of PA and IPA as morphology adjust control agent, using strontium chloride hexahydrate ($SrCl_2·6H_2O$) and anhydrous sodium carbonate (Na_2CO_3) as the starting materials. The influence of structure of carboxylic acid on morphology was investigated.

2. Experimental

2.1. Materials

All the chemicals used to prepare reactant solutions, $SrCl_2·6H_2O$, Na_2CO_3, phthalic acid (PA), isophthalic acid (IPA) were analytical grade, commercially obtained and used without further purification. Ultrapure water was used throughout the experiment.

2.2. Preparation of $SrCO_3$

The 0 mg (0 mmol), 34.2 mg (0.205 mmol), 62.0 mg (0.369 mmol), 88.5 mg (0.533mmol) IPA were added into five 50 mL beakers with 10 mL ultrapure water, respectively. Then, 0 mg (0 mmol), 22.0 mg (0.205 mmol), 39.0 mg (0.369 mmol), 56.8 mg (0.533 mmol) Na_2CO_3 were added into each beaker under stirring. After the mixture solutions were stirred for 10 min. 111.0 g (1.0 mmol) $SrCl_2·6H_2O$ was added into each beaker under stirring. Then, 0.1060 g (1.0 mmol) Na_2CO_3 was added into each beaker. The precipitates produced were separated by centrifugation, washed three times with ultrapure water and anhydrous ethanol, and then vacuum dried at 40℃ for about 48 h. The size and morphologies of the particles were examined by SEM. The crystal phases were determined by FT-IR spectroscopy and powder X-ray diffractometer. Using PA as crystal growth adjuster to preparing $SrCO_3$, procedure and the amount of reactants are the same as using IPA as adjuster expect that IPA was replaced by PA.

2.3. Characterization

The as-prepared samples were characterized by X-ray diffraction (XRD) analysis using an X-ray diffractometer (Model Bruker D8 ADVANCE) with Cu-Kα1 (λ=1.54178 Å) monochromatized radiation at 40 kV and 40 mA. The samples were scanned over a 2θ range of 20-70 ° at a step size of 0.02°. The size and morphologies of the samples were examined by a scanning electron microscope (SEM) (JEOL JSM 5600LV) with gold coating. The Fourier transform infrared (FT-IR) spectroscopy on a Nicolet 6700 FT-IR spectrophotometer by using KBr pellet in the range of 4000~400 cm^{-1} and 32 scans were collected at a resolution of 4 cm^{-1}.

3. Results and discussion

The products prepared using $SrCl_2·6H_2O$ and Na_2CO_3 as precursor in the 10.0 mL water solution were first examined by XRD, and the XRD patterns are shown in figure 1 and figure 2. All diffraction peaks of the product can be indexed as the (111), (002), (112), (220), (221), (132), (113) reflections of a pure strontianite-type crystal [9], indicating that $SrCO_3$ crystal was formed. The samples consisted of a single phase of well-crystalline $SrCO_3$ with an orthorhombic structure (PDF 05-0418) and with lattice parameters of a) 5.107 Å, b) 8.414 Å, c) 6.029 Å. No peaks from impurities were observed, showing pure strontianite-type crystal according to the XRD standard spectrum of $SrCO_3$ crystal. But in figure 1 and figure 2, compared with sample 1, the diffraction peaks of samples 2, 3, 4, 5, 6, 7 broaden obviously. The broadening features of the samples implied that the crystals could be composed of primary nanoparticles [26].

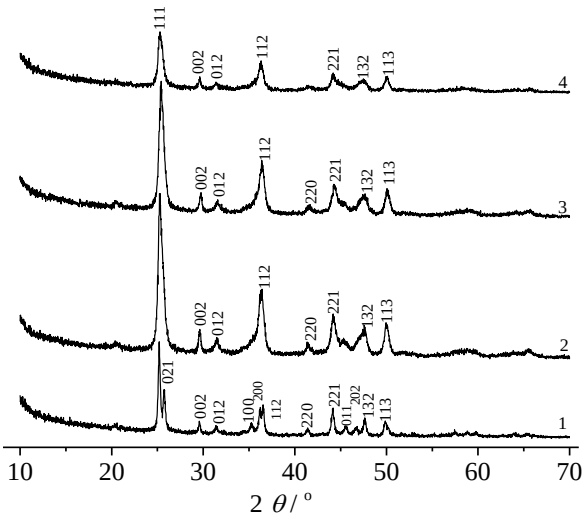


Figure 1. XRD patterns of the as-synthesized samples in the presence of IPA (mg): 1: 0.0; 2: 34.2; 3: 62.0; 4: 88.5.

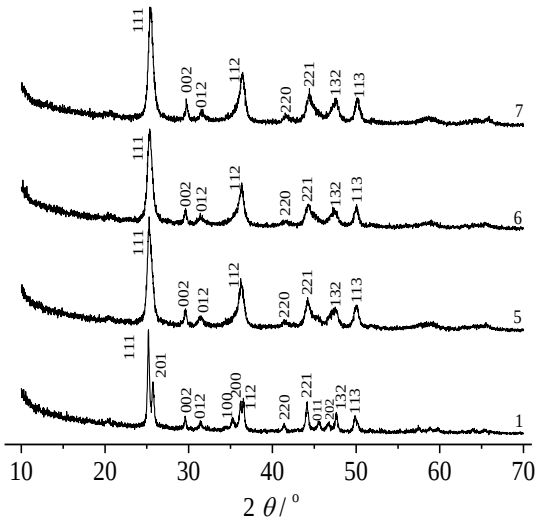


Figure 2. XRD patterns of the as-synthesized samples in the presence of PA (mg): 1: 0.0; 5: 34.2; 6: 62.0; 7: 88.5.

The FT-IR spectrum is a strong tool for characterizing inorganic minerals. The IR spectra of the samples are shown in figure 3 and figure 4. Isolated planar CO_3^{2-} anion has a D_{3h} symmetry [27]. The absorption bands attributed to the vibrations in CO_3^{2-} anion are located range from 1800 to 400 cm^{-1}. The IR spectra of the samples represent the characteristic absorbance of $SrCO_3$ particles. The strong broad absorption centered at about 1465 cm^{-1} is assigned with the asymmetric stretching vibrations, and the strong sharp absorption band at 856 cm^{-1} and 706 cm^{-1} can be assigned to the bending out of plane vibrations and in plane vibrations [28], respectively, which provide further evidence for the pure $SrCO_3$ composition of the product. This conclusion is in agreement with the result from the XRD pattern shown in figure 1 and figure 2.

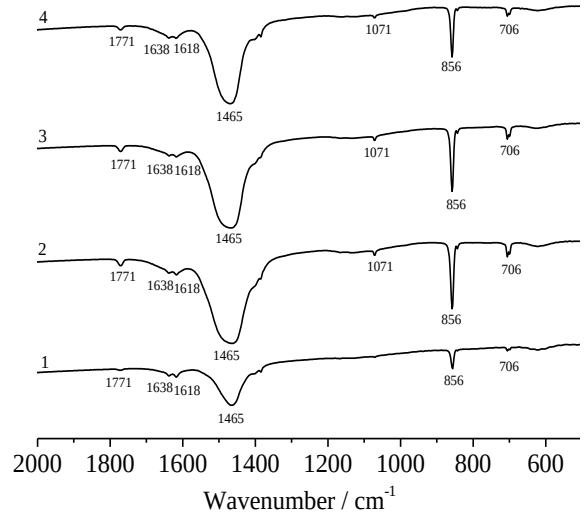


Figure 3. The FT-IR spectra of the as-synthesized samples in the presence of IPA (mg): 1: 0.0; 2: 34.2; 3: 62.0; 4: 88.5.

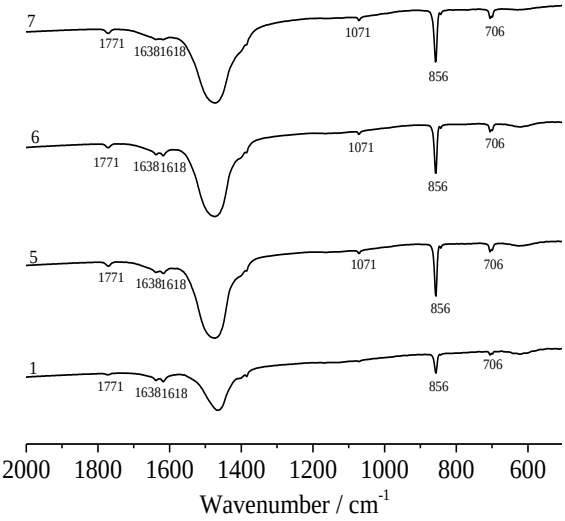


Figure 4. The FT-IR spectra of the as-synthesized samples in the presence of PA (mg): 1: 0.0; 5: 34.2; 6: 62.0; 7: 88.5.

The morphologies of all samples were further investigated by SEM and compiled in figure 5 (without and with the exist of IPA) and figure 6 (using PA as adjuster). The as-obtained $SrCO_3$ particles without IPA or PA (shown in figure 5-1) appear the uniformed morphology of spindle shape

with big length/diameter ratio of 3/1 and have good dispersion. When different amounts of IPA were added into the liquid phase preparation system, the morphologies of $SrCO_3$ particles are flower-like clusters formed by the assembling of short rod whisker (figure 5-2). The majority of clusters are center-bundled and two ends emission growing shape which are like two beams of flower bundled reversely together. Some clusters are like a beam of flower. In addition, the sizes of clusters and short rods are the smallest when the addition amount of IPA is 62.0 mg (figure 5-3).

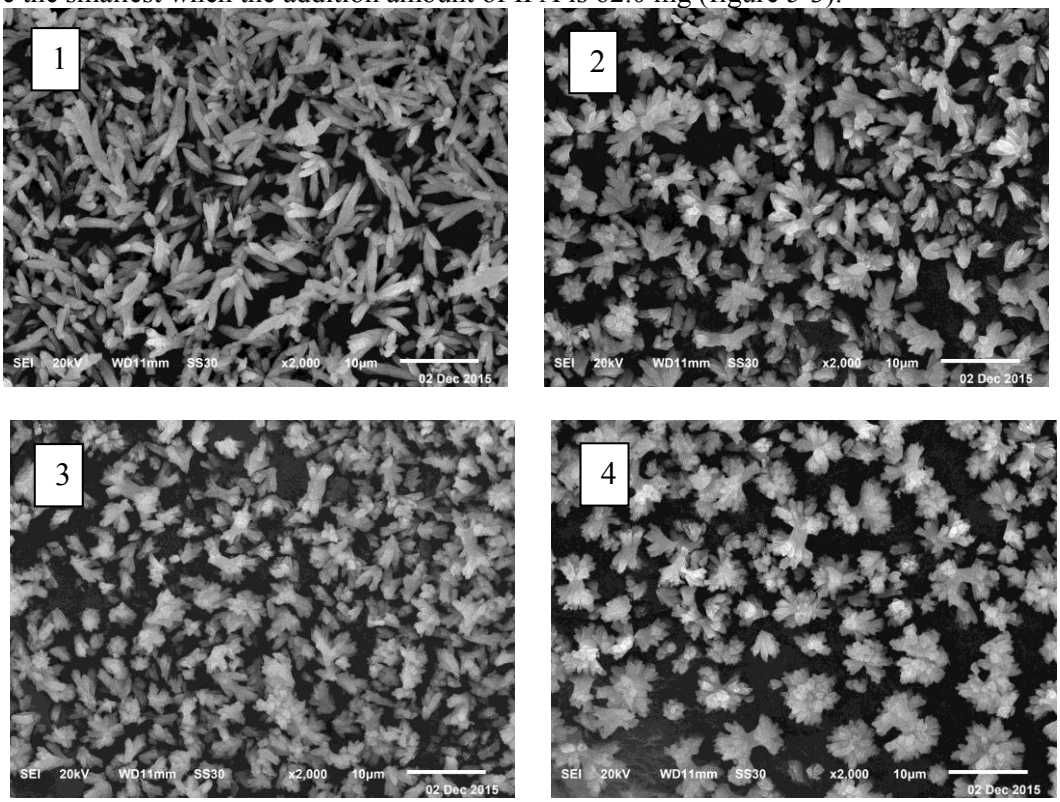


Figure 5. SEM images of the as-synthesized samples in the presence of IPA (mg): 1: 0.0; 2: 34.2; 3: 62.0; 4: 88.5.

Figure 6 shows the SEM images of $SrCO_3$ particles prepared in the presence of PA. When the adding amount of PA is 34.2 mg, figure 6-5 shows that $SrCO_3$ particles prepared are frost flower-like clusters. The magnified SEM image in Fig.6-5 (insert) indicates that each cluster is assembled with numerous well-aligned needle-like whisker, which is different from the self-assembling of short rod whiskers (figure 5-4). When the amount of PA is elevated to 62.0 mg, it is obvious that $SrCO_3$ particles have smaller size and better dispersion by contrasting to figure 6-5 and figure 6-6. The amplified SEM image (insert in figure 6-6) reveals that most $SrCO_3$ clusters are carnation flower-shaped clusters assembled with needle-like whisker and the overall appearance of clusters has two types. One is like two beams of carnation flower bundled reversely together, the other is like a beam of carnation flower. figure 6-7 shows the SEM image of $SrCO_3$ prepared with 88.5 mg of PA, which can be seen that the particles size become big again and the morphology change into irregular sphere without exist of needle-like whisker on the outside surface. To sum up, the adding amount of PA has noteworthy effects on the size, morphology and dispersion of $SrCO_3$ particles.

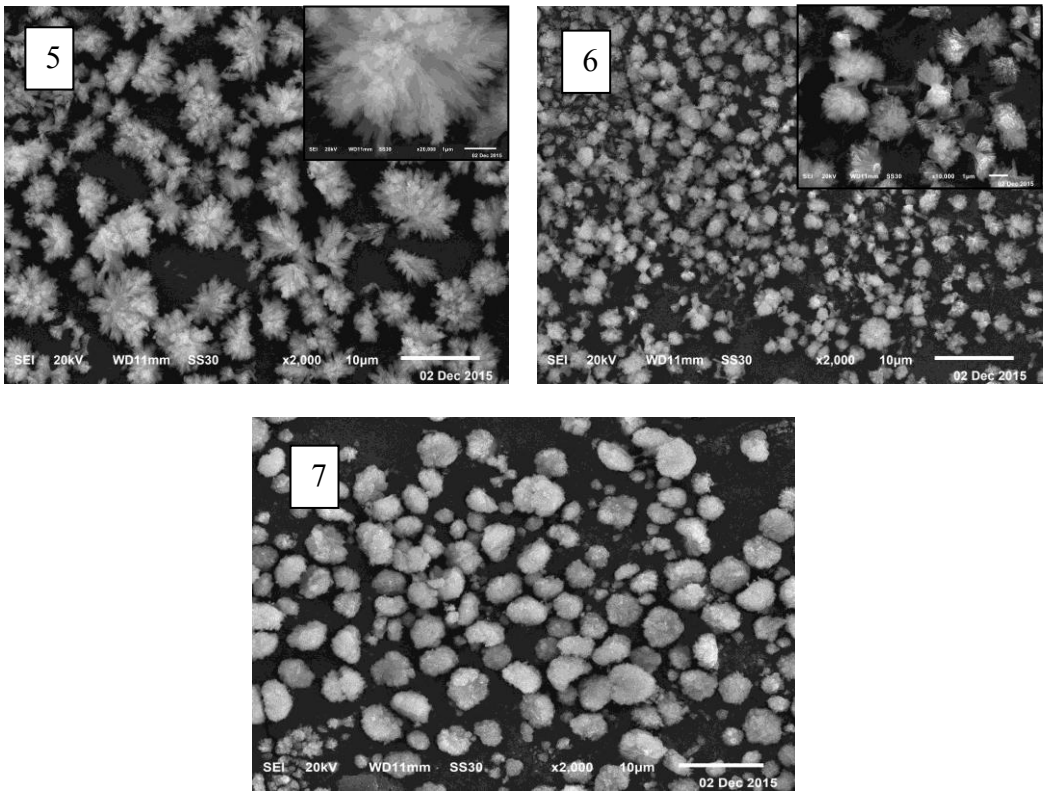


Figure 6. SEM images of the as-synthesized samples in the presence of IPA (mg): 1: 0.0; 5: 34.2; 6: 62.0; 7: 88.5.

It is well known that IPA and PA have strong coordination ability with Sr^{2+} ion. In the presence of IPA and PA, the complexes of $Sr(IPA)_m^{n-}$ or $Sr(PA)_m^{n-}$ formed due to the strong coordination ability of IPA and PA. But when Na_2CO_3 is added, dissociated Sr^{2+} can react with CO_3^{2-} species spontaneously to form the SrCO3 nuclei at room temperature because of small solubility product of $SrCO_3$ (at 25 °C, $K^{\Theta}_{sp} = 1.1\times10^{-10}$). Then the $SrCO_3$ nuclei grew to form nanocrystals.

The negatively charged groups of $-COO^-$ of PA or IPA molecules can bind Sr^{2+} strongly. Therefore, PA and IPA molecules can act as capping agents which selectively bind to facet(s) on a nanocrystal or microcrystal to alter their specific surface free energies. At the same time, the capping agent chemisorbed on a facet will hinder or prevent the deposition of ions onto this facet. The facet covered by the capping agent will take a slower growth rate and thus a greater proportion on the surface. This in turn changes both the edge-step free energies and the shape of the steps. Changes in step shape directly modify the macroscopic crystal shape by inducing the formation of new crystal faces resulting in macroscopic morphological modifications [29]. The distances between two carboxylate groups of PA and those of IPA are different, which mean that carboxylate groups of PA and IPA may bind different crystal face(s) of $SrCO_3$ particles, which result in the formation of crystals with different morphologies.

4. Conclusions

$SrCO_3$ crystals with various morphologies were prepared using PA and IPA as crystal growth adjusters, respectively. When IPA was used as adjuster, the major morphologies of $SrCO_3$ are center-bundled and two ends emission growing clusters formed by the self-assembling of short rod whiskers. While using PA as adjuster, flower-like $SrCO_3$ clusters are assembled by needle-shaped whiskers and their morphologies change from flower shape to sphere shape with the increasing of PA amount. The result indicates that the morphology of $SrCO_3$ may be adjusted by the structure of carboxylic acid.

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