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

Yuxi Liu, Xianghai Jing, Xianhong Hu and Gang Wu
College of Material and Chemical Engineering, Chu Zhou University, Chu Zhou 239012, P. R. China
liuyuxiemail@126.com

Abstract. SrCO₃ crystals with various morphologies were prepared using precipitation method by the reaction of Na₂CO₃ and SrCl₂ 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 SrCO₃ 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 SrCO₃ 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 SrCO₃ 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 SrCO₃, strontianite, 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, pyrotechnics, a precursor for various strontium compounds, and as a catalyst [3-6]. Therefore, SrCO₃ 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 SrCO₃ (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 SrCO₃ 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 SrCO₃ 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 SrCO₃ in the presence of nonionic/anionic surfactants F127/SDS in the water or alcohol. SrCO₃ particles change from pancakes to flowers, and then to irregular flakes [24].
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$_2$O) and anhydrous sodium carbonate (Na$_2$CO$_3$) 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$_2$O, Na$_2$CO$_3$, 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 (0.533 mmol) 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$_2$CO$_3$ 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$_2$O was added into each beaker under stirring. Then, 0.1060 g (1.0 mmol) Na$_2$CO$_3$ 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°C 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$_2$O and Na$_2$CO$_3$ 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].
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.

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.
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$_2$CO$_3$ is added, dissociated Sr$^{2+}$ can react with CO$_3^{2-}$ species spontaneously to form the SrCO$_3$ nuclei at room temperature because of small solubility product of SrCO$_3$ (at 25 °C, $K_{sp}^\Theta = 1.1 \times 10^{-10}$). 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.
Acknowledgements
This work was financially supported by, The Natural Science General Subject of An Hui Education Department (KJ2015B14), Scientific Research Starting Foundation (2016qd04) and National Training Program of Innovation and Entrepreneurship for Undergraduates (201710377023) for financial support of this work.

References
[1] Bao S P, Chen X Y, Li Z, Yang B J and Wu Y C 2011 Cryst. Eng. Comm. 13 2511
[2] Li Y, Cao M H and Feng L Y 2009 Langmuir 25 1705
[3] Zhang Y Y, Liu J L, Zhu Y X, Shang Y, Yu M and Huang X J 2009 Mater. Sci. 44 3364
[4] Suryanarayanan V, Nair A S and Tom R T 2004 J. Mater. Chem. 14 2661
[5] Homeijer S J, Barrett R A and Gower L B 2010 Cryst. Growth Des. 10 1040
[6] Wu W K, Ma Y R, Xing Y, Zhang Y Z, Yang H, Luo Q, Wang J, Li B and Qi L M 2015 Cryst. Growth Des. 15 2156
[7] Oldenberg S J, Averitt R D, Westcott S L and Halas N J 1998 Chem. Phy. Lett. 288 243
[8] Liz-Marzan L M, Giersig M and Mulvaney P 1996 Langmuir 12 4329
[9] Du J M, Liu Z M, Li Z H, Han B X, Huang Y and Zhang J L 2005 Microporous and Mesoporous Mater. 83 145
[10] Sondi I and Matijević E 2003 Chem. Mater. 15 1322
[11] Küther J, Bartz M, Seshadri R, Vaughan G B M and Tremela W 2001 J. Mater. Chem. 11 50
[12] Li S Z, Zhang H, Xu J and Yang D R 2005 Mater. Lett. 59 420
[13] Huang Q, Gao L, Cai Y and Aldinger F 2004 Chem. Lett. 33 290
[14] Cao M H, Wu X L, He X Y and Hu C W 2005 Langmuir 21 6093
[15] Rautaray D, Sanyal A, Adyanthaya S D, Ahmad A and Sastry M 2004 Langmuir 20 6827
[16] Balz M, Therese H A, Kappl M, Nasdala L, Hofmeister W, Butt H J and Tremel W 2005 Langmuir 21 3981
[17] Ma M G and Zhu Y J 2007 J. Nanosci. Nanotechno. 7 4552
[18] Xu S J and Wu P Y 2014 Cryst. Eng. Comm. 16 1311
[19] Rautaray D, Sainkar S R and Sastry M 2003 Langmuir 19 888
[20] Lu Y, Yin Y D, Li Z Y and Xia Y N 2002 Nano Lett. 2 785
[21] Caruso R A and Antonietti M 2001 Chem. Mater. 13 3272
[22] Schuetzand P and Caruso F 2002 Chem. Mater. 14 4509
[23] Yu J G, Guo H and Cheng B 2006 J. Solid State Chem. 179 800
[24] Guo G L, Yan G W, Wang L and Huang J H 2008 Mater. Lett. 62 4018
[25] Zhu W C, Zhang G L, Li J, Zhang Q, Piao X L and Zhu S L 2010 Cryst. Eng. Comm. 12 1795
[26] You C, Zhang Q, Jiao Q Z and Fu Z D 2009 Cryst. Growth Des. 9 4720
[27] Miller F A, Carlson G L, Bentley F F and Jones W H 1960 Spectrochimica Acta 16 135
[28] Alavi M A and Morsali A 2010 Ultrason. Sonochem. 17 132
[29] Orme C A, Noy A, Wierzbički A, McBride M T, Grantham M, Teng H H, Dove P M and DeYoreo 2001 J. J. Nature 411 775