

Shape evolution of SrCO₃ particles in the presence of poly-(styrene-alt-maleic acid)

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Abstract

In this paper, strontium carbonate particles with different morphologies were prepared by a simple precipitation reaction of sodium carbonate with strontium nitrate in the absence and presence of poly-(styrene-alt-maleic acid) (PSMA). The as-prepared products were characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD). The effects of the concentration of PSMA on the morphologies and phase structures of strontium carbonate particles were investigated and discussed. The results showed that SrCO₃ particles with various shapes, such as bundles, dumbbells, irregular aggregates and spheres could be obtained by varying the concentration of PSMA. A schematic illustration was proposed to account for the shape evolution of the as-prepared SrCO₃ particles.

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1. Introduction

The controlled synthesis of inorganic or inorganic/organic hybrid materials with specific size, shape, and crystal structure is a key aspect of modern materials science in many fields such as, advanced materials, catalysis, medicine, electronics, ceramics, pigments, cosmetics, etc. [1–5]. Compared with the size control, the morphology control has been much more difficult and demanding to achieve by means of classical colloid chemistry [6]. In biological systems, however, biomacromolecules are used as nucleators, cooperative modifiers, and matrixes or molds to exert exquisite control over the processes of biomineralization, which results in unique inorganic–organic composites (e.g., seashells, bones, teeth, and many others) with various special morphologies and functions [7–13].

As far as strontium carbonate is concerned, the mineral itself is an important raw material in modern electronic

industry [14]. Furthermore, strontium carbonate has only one crystal-phase, so it has been widely studied as a model system for bio-crystallization [15–20]. Some ordered systems, such as self-assembly monolayers [15–17], thermo-evaporated stearic membrane [18,19] and polyanionic additives [20], etc. were designed to induce the crystallization of SrCO₃ from aqueous solution. Recent work carried out in our group showed that poly-(styrene-alt-maleic acid) (PSMA) could exert a strong influence on external morphology and/or crystalline structure of inorganic particle of calcium carbonate [11] and calcium oxalate [21]. In order to investigate the availability and functionality of PSMA on the morphological control of other crystals, further studies needed to be conducted. As a part of a series of works, PSMA was used as a crystal modifier to adjust the morphology of SrCO₃ particles by varying the concentration of PSMA. It was found that different shapes of SrCO₃ particles could be successfully obtained. This work may provide new insights into the morphological control of SrCO₃ particles and the controllable synthesis of other novel inorganic materials.

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2. Experimental

2.1. Preparation

PSMA (sodium salt, 30 wt% solution in water, average molecular weight $\sim 120,000$) was obtained from Aldrich. All other chemicals were of A.R. grade and used without further purification. The water used in the experiment was distilled water. In a typical synthesis, a solution of Na_2CO_3 (0.5 M, 0.4 mL) was added into an aqueous solution of PSMA (100 mL, containing different amount of PSMA according to the needs of experiments), and the pH value of the solution was adjusted to 10 by adding HCl (1 M) or NaOH (1 M) solution. Then a solution of $\text{Sr}(\text{NO}_3)_2$ (0.5 M, 0.4 mL) was added quickly into the pH-adjusted solution under vigorous stirring by using a magnetic stirrer. The mixture was stirred for another 5 min, and then the solution was kept under static conditions for 24 h to ensure reaction equilibration.

2.2. Characterization

The resulting SrCO_3 precipitates were characterized by scanning electron microscopy (SEM) (type JSM-5610LV, Japan) with an accelerating voltage of 20 kV. The powder X-ray diffraction (XRD) patterns obtained on an HZG41B-PC X-ray diffractometer using $\text{CuK}\alpha$ radiation at a scan rate of $0.05^\circ 2\theta \text{S}^{-1}$ were used to determine the identity of any phase present and their crystallite size. The accelerating voltage and the applied current were 35 kV and 20 mA, respectively.

3. Results and discussion

Fig. 1 shows SEM micrographs of SrCO_3 particles obtained from aqueous solution in the absence and presence of PSMA at room temperature. It could be seen from Fig. 1a that, in the absence of PSMA, the as-obtained particles appeared bundle-like aggregates consisting of many small SrCO_3 needles aligned radially towards both ends. Further observation showed that there existed many fragments ruptured at the middle parts of the bundles. Therefore, it could be inferred that the middle parts of the bundles were more fragile than their radial branches. When a small amount of PSMA (0.01 g L^{-1}) was added into the reaction system, the morphology of SrCO_3 particles was obviously changed (as shown in Fig. 1b). Compared with the above-mentioned bundle-like aggregates, the morphology of the as-obtained particles was more homogeneous whatever in shape or in size, which looked like a dumbbell. Such monodispersed morphology was a bit different from that observed by Qi and coworkers [20]. The formation of such a shape in our work might be due to the oriented adsorption of PSMA on some specific crystal faces perpendicular to the growth direction of the needle-like branches, which inhibited the growth of the needles. Moreover, some projections at the both ends of particles

can be easily found. At $[\text{PSMA}] = 0.02 \text{ g L}^{-1}$, the ends of the dumbbells became large (as shown in Fig. 1c). When the concentration of PSMA was further increased to 0.1 g L^{-1} , spherical particles with concave surfaces were prepared (as shown in Fig. 1d). When the concentration of PSMA reached 0.3 g L^{-1} , perfect spherical particles were obtained (Fig. 1e). Lots of investigations carried out in our group have shown that when the concentration of organic additives, acted as shape modifier, reached a critical value, the final shape of the controlled particles tended to become a sphere [4,5,15,21–23]. This might be due to the fact that, when the concentration of additives reached an enough amount, the oriented adsorption of additives would disappear, which resulted in the formation of a sphere [22–24]. It could be seen from Fig. 1a to e that the size of the spherical particles was obviously larger than that of those obtained in other conditions. This might be ascribed to the decrease of the number of nucleation at a high PSMA concentration due to the fact that most of the ions for nucleation or growth were adsorbed by PSMA, which resulted in the formation of big spherical particles.

In order to investigate the influence of PSMA on the phase structures of SrCO_3 particles, three samples were selected for XRD characterization and the XRD results were shown in Fig. 2. It could be seen that XRD patterns of SrCO_3 products prepared at different PSMA concentration had the same diffraction patterns. This was due to the fact that strontium carbonate is single-phase crystal. Further observation showed that with increasing the amount of PSMA, the intensity of diffraction peaks decreased and the crystallization became weak. This could be attributed to the fact that PSMA inhibited the crystallization and growth of SrCO_3 particles by adsorbing on the crystal faces. We measured the amount of SrCO_3 precipitates obtained in the presence of 0, 0.01 and 0.3 g L^{-1} PSMA by using a mass analysis method and found that their mass was 0.285, 0.250 and 0.120 g L^{-1} , respectively. This also showed that PSMA could inhibit the formation and crystallization of SrCO_3 particles due to PSMA adsorbing Ca^{2+} ions [11]. Using line-broadening methods and Scherrer's equation [25], the average crystallite sizes of SrCO_3 particles were calculated. It was found that those of SrCO_3 particles obtained in the presence of 0, 0.01 and 0.3 g L^{-1} PSMA were 63, 36 and 11 nm, respectively. This also indicated that with increasing the amount of PSMA, the crystallite size of SrCO_3 particles decreased.

Qi et al. has ever proposed a schematic growth mechanism for the formation of oval-, peanut-, and peach-like BaSO_4 particles [10], but this mechanism does not coincide well with our experimental results, probably due to the difference in crystal habit between BaSO_4 and SrCO_3 . Fig. 3 shows a schematic mechanism of formation of SrCO_3 particles obtained in the presence of PSMA. At first, amorphous nanoparticles were formed in the presence of PSMA. Then the nanoparticles aggregated and evolved into small crystals with high surface energy marked by

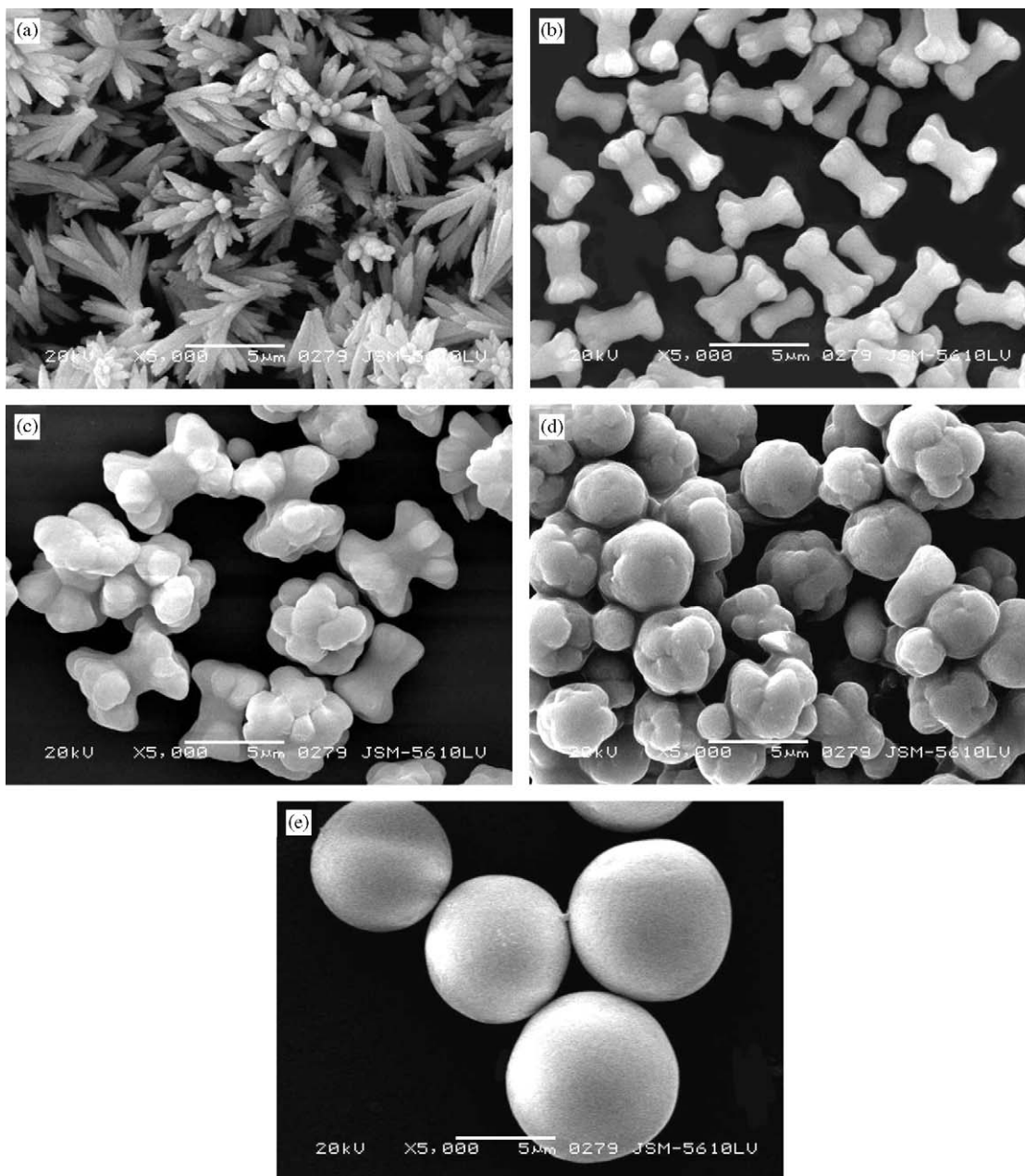


Fig. 1. SEM micrographs of SrCO_3 particles obtained in the presence of PSMA at room temperature, $[\text{SrCO}_3] = 2\text{ mM}$, $\text{pH} = 10$, $[\text{PSMA}] =$ (a) 0, (b) 0.01, (c) 0.02, (d) 0.1 and (e) 0.3 g L^{-1} .

arrows (a). In the absence of PSMA, the growth rate of these end faces was higher than that of the side faces, which resulted in the formation of the bundles (Fig. 3(b)). In the presence of PSMA, carboxylic groups of PSMA might adsorb on these high-energy faces and inhibited their growth, and side faces gradually became growth faces. This resulted in the formation of dumbbells (c) and (d) and spherical particles (e) and (f). The morphology variation of SrCO_3 particles with varying polymer concentration might be ascribed to the different adsorptive feature of PSMA on the crystal plane of SrCO_3 . It is known that the exposed faces of crystals show different polarity pattern and average interface energy, and thus adsorb the polymer

with different efficiency [24]. At a lower concentration, the polymer just selectively adsorbs on a certain crystal face of SrCO_3 , leading to the anisotropic growth and directional assembly. In contrast, at a higher concentration, the polymer is enough to adsorb on almost all the crystal faces, resulting in the formation of spherical superstructure [22,24].

Usually, most of the carbonates are easy to dissolve (or decompose) in a low pH value solution (or a acidic condition). Hence, carbonate particles with novel morphologies can be used as rigid templates for the preparation of other inorganic particle material with hollow structures and novel morphologies. Although the reports on using

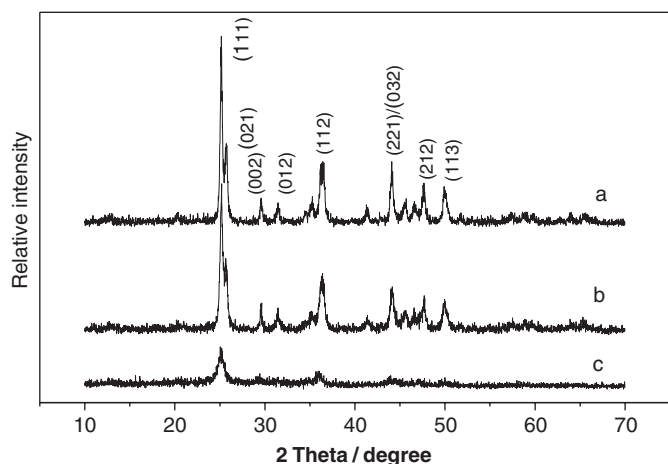


Fig. 2. XRD patterns of SrCO_3 particles obtained in the presence of PSMA: $[\text{SrCO}_3] = 2 \text{ mM}$, $\text{pH} = 10$, $[\text{PSMA}] =$ (a) 0, (b) 0.01 and (c) 0.3 g L^{-1} .

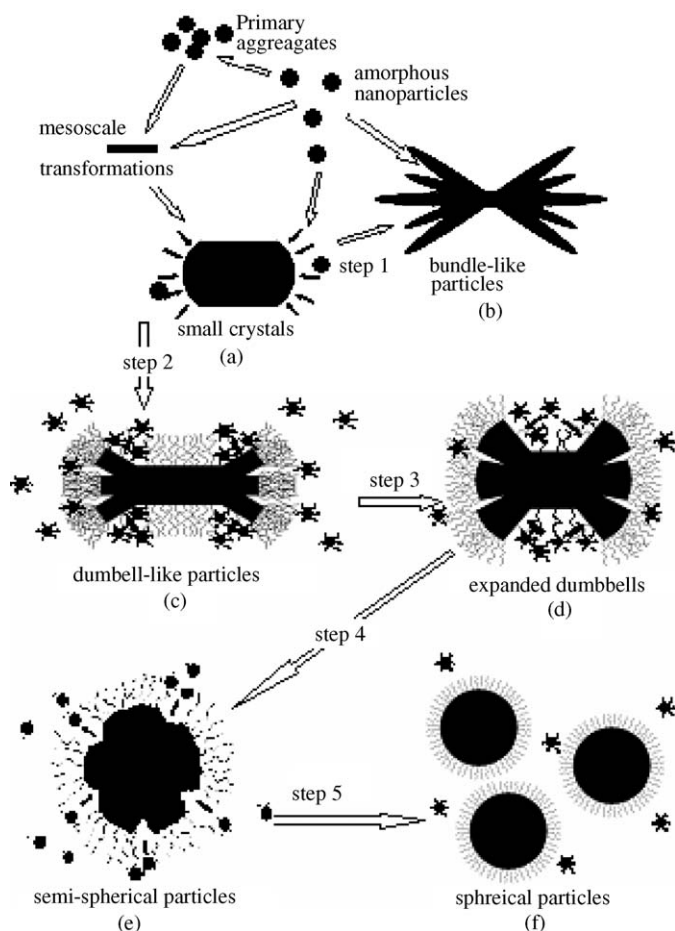


Fig. 3. Schematic mechanism of formation of SrCO_3 particles obtained in the presence of PSMA.

carbonate particles with novel shapes as rigid templates for the synthesis of other novel inorganic particle materials were limited till now, we believe the use of novel-shaped carbonate particles as rigid templates will be promising in

the future. Furthermore, carbonate particles with novel morphologies will also find their wide application in such industrial fields as paper, rubber, plastics, paint, etc. [5].

4. Conclusions

The presence of organic macromolecules played an important role in controlling the morphology of SrCO_3 particles. The shape evolution of SrCO_3 particles from bundle-like aggregates to dumbbells and perfect spherical particles were observed one by one with increasing the concentration of PSMA. Such a shape evolution might provide new insights into the morphological control of SrCO_3 particles and the controllable synthesis of other novel inorganic materials.

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