Facile synthesis of SrCO₃ nanostructures in methanol/water solution without additives

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Abstract

Highly dispersive strontium carbonate (SrCO₃) nanostructures with uniform dumbbell, ellipsoid, and rod-like morphologies were synthesized in methanol solution without any additives. These SrCO₃ were characterized by X-ray diffraction, field emission scanning electron microscopy, and N₂ adsorption-desorption. The results showed that the reaction temperature and the methanol/water ratio had important effects on the morphologies of SrCO₃ particles. The dumbbell-like SrCO₃ exhibited a Broader-Emmett-Teller surface area of 14.9 m² g⁻¹ and an average pore size of about 32 nm with narrow pore size distribution. The formation mechanism of the SrCO₃ crystal was preliminary presented.

Keywords: Nanoparticle, Crystallization, SrCO₃, Refluxing

Background

Recently, nanomaterials with different morphologies have attracted great attention for their promising applications such as optical materials, efficient catalysts, drug-delivery carriers [1-3], etc. Strontium carbonate (SrCO₃) is one of the important reagents used in firework, pigment, and electron manufacturing [4]. There are two main usages of SrCO₃: they are used in the production of cathode ray tubes and ferrite magnets for small direct-current motors [5]. However, SrCO₃ with different morphologies may own different potential usages. For example, SrCO₃ with a needle-like crystal is used in optical polymers to reduce birefringent phenomena [6]. A sphere-shaped crystal with a diameter less than 1 μm is favorable for high-temperature electric components. So far, SrCO₃ with various morphologies such as hierarchical branches, hexagonal prisms, straw-like, pancake, ellipsoid, needle, flower ribbon, bundle, dumbbell, sphere, and rod-like have been reported [5,7-13]. Various methods have been reported on the preparation of SrCO₃ nanostructures including hydrothermal [14], microwave-assisted [9], microemulsion-mediated solvothermal methods [5], etc. Although nanoscale SrCO₃ with special morphologies was obtained, the preparation processes were complex and strict, such as high-pressure, high-temperature, and tedious synthetic procedures as well as high cost were required. Aside from that, large-scale synthesis of SrCO₃ nanostructures still remains a considerable challenge.

In this work, a new facile way was reported to synthesize SrCO₃ nanostructures by continuously carbonizing Sr(OH)₂ with CO₂ in methanol/water solution without additives. The effects of the reaction temperature and the methanol/water (m/w) molar ratio on the morphology evolution were investigated. This method is simple, low-cost, and easy to control in producing large-scale monodisperse SrCO₃ nanostructures.

Methods

Sr(OH)₂·8H₂O was purchased from Alfa Aesar (Ward Hill, MA, USA). Other reagents were purchased from Beijing Reagents Co., Ltd. (Beijing, China). All reagents used in our experiments were of analytical grade. Experiments were carried out in a 150-ml reactor with a refluxing system. The reaction temperature was controlled using a thermostatic bath, as shown in Figure 1.

In the typical experiment, several grams of Sr(OH)₂·8H₂O were dissolved into the methanol/water solution and kept at room temperature for 24 h. The concentration of the solution was kept at 0.05 mol l⁻¹ for all the experiments. The solution was put into the reactor and stirred using a propeller agitator with a speed of about 800 rpm. Mixed CO₂ of 100 ml min⁻¹ (80 ml min⁻¹ N₂ + 20 ml min⁻¹ CO₂) was induced into the reactor and lasted for 30 min. Then, the gas was cut off and continuously agitated for...
another 2 h. Finally, the solution was naturally cooled to room temperature. The products were separated by centrifugation and washed with deionized water and ethanol alternately for three times. The obtained carbonate samples were dried at 60°C for 24 h.

The products were characterized by field emission scanning electron microscopy (FESEM; JSM-6700 F, JEOL, Akishima-shi, Japan) and X-ray diffraction (XRD; XPert PRO MPD, PANalytical B.V., Almelo, The Netherlands); patterns of carbonate were recorded on a diffractometer (using Cu Kα radiation; λ = 0.154 nm) operating at 40 kV/30 mA. A scanning rate of 0.2° s⁻¹ was applied to record the patterns. The N₂ adsorption-desorption isotherms were measured at 77 K using an automated surface area and pore size analyzer (QUADRASORB SI-MP, Quantachrome Instruments, Boynton Beach, FL, USA).

**Results and discussion**

The XRD patterns in Figure 2 confirm the SrCO₃ obtained by carbonating Sr(OH)₂ with CO₂ in the methanol/water system. All peaks in these patterns can be indexed as orthorhombic phase (JCPDS No. 84–0418) with lattice constants \(a = 5.107 \text{ Å}, b = 8.414 \text{ Å}, c = 6.029 \text{ Å}; \alpha = \beta = \gamma = 90\). By comparing the XRD patterns of the as-synthesized SrCO₃ crystal with the standard, diffraction peaks located in 2θ (in degrees) of 20.53, 25.35, 29.71, 31.59, 36.41, 41.42, 44.36, 47.39, and 50.10 are readily indexed as the (111), (110), (021), (102), (200), (041), (221), (220), (232), (043), and (113) planes for SrCO₃, respectively. The XRD results indicate that the SrCO₃ nanomaterials are well crystallized, and no impurity species are found.

From the XRD pattern, we can know that the SrCO₃ from the pure methanol solution have poor crystallinity than those from the methanol/water solution (Figure 2; some crystal planes such as (021), (102), and (200) are only observed in the SrCO₃ from the methanol/water solution. The results indicate that the SrCO₃ from the methanol/water solution has better developed crystal plane.

The morphologies of the products characterized by FESEM were shown in Figures 3 and 4. Figure 3 shows the morphology evolution of the products obtained at different temperatures in pure methanol. All these products have characteristics of being highly monodisperse and uniform. Ellipsoidal particles with a long axis of 350 nm and a short axis of 180 nm were obtained when a reaction temperature of 70°C was presented (Figure 3A). As the temperature was decreased to 60°C, the products were rod-like with a diameter of 110 nm and a length of about 250 nm. However, some particles have a trend to swell up, turning into dumbbell-like (Figure 3B inset). Finally, when 50°C was presented, uniform dumbbell-like particles with a handle diameter of 160 nm and a top diameter of about 200 nm were observed, and the length of the particles is about 340 nm (Figure 3C). It is obvious that these dumbbell-like particles are constructed by small nanocrystallites with a diameter of about 20 nm (Figure 3C inset). The particles seem to have a mesoporous structure, which will be confirmed by the results of the N₂ adsorption-desorption measurement later.

In order to investigate the effect of the m/w ratio on the morphology of SrCO₃, the crystals were prepared in m/w ratios of 3:2, 1:1, and 2:3. Figure 4 shows the morphologies of the products from the different m/w ratios. It is interesting that the rod-like SrCO₃ with different length-diameter ratios were observed in most
cases. The results indicated that the m/w ratio has a great effect on the morphology of products. When the ratio of m/w is 3:2 (Figure 4A), irregular plate-like products with a few short rods have been observed in the picture; the rods had a diameter of 90 nm and a length of 600 nm. As the m/w ratio was changed to 1:1, mono-disperse rod-like products with a diameter of 120 nm and a length of 1.2 μm were observed (Figure 4B). When the m/w ratio is 2:3, the morphologies (Figure 4C) of the products were similar with those obtained in the m/w
ratio of 1:1; it seems that the crystallinity of the products is better than that of Figure 4B.

The high porosity properties of the dumbbell-like SrCO₃ products were confirmed by the measurement of the Brunauer-Emmett-Teller (BET) surface area and the N₂ adsorption-desorption isotherms (Figure 5). The BET specific surface area is 14.9 m² g⁻¹, which is smaller than those of the mesoporous SrCO₃ [15] and hierarchical mesoporous SrCO₃ submicron spheres [16]. The reason can be ascribed to the relative larger diameter of the constructing particles and the larger total pore volume of 0.18 cm³ g⁻¹. According to IUPAC recommendations [17], the observed hysteresis of the dumbbell-like product was a characteristic of a type III isotherm with a type H3 hysteresis loop in the $P/P_0 > 0.8$. This means that the mesopores in the reign size of 12 to 32 nm were presented (Figure 5 inset). Moreover, the observed hysteresis loop near to $P/P_0 \approx 1$ suggests that pores >50 nm were also presented [18]. This may be explained that mesopores of 12 to 32 nm ascribed to the auto-assembled stacks of uniform nanosphere, while the large pores >50 nm attributed to the aggregation of the dumbbell-like particles. It was reported that materials with a mesoporous structure possessed higher chemical reactivity due to their higher mass transportation performance [19].

Although the exact formation mechanism of these morphologies of the SrCO₃ crystal is still not clear at present, our results show that the reaction temperature and the m/w ratio have great effects on the morphology. The m/w ratio or the polarity of the mixed solvent had a great effect on the morphology which had been reported by Lou et al. [17] and Zhang et al. [20]. Studies showed that alcohols can affect the dielectric constant of the medium and change the crystal growth rate [21]. When pure methanol was presented, the -OH of methanol might adsorb to the nuclei of the crystals and change its surface energy and then the morphology of the products. As the temperature was increased, the vibration of -OH groups in methanol was more rapid and absorption effects were weakened [22]. Thus, the morphology of the product has little change at relatively high temperatures of 60°C and 70°C (Figure 3A,B). However, when the methanol/water solution was presented, the forming hydrogen bond between methanol and water prevented the absorption to the nuclei, and rod-like products growing along the c-axis were obtained.

**Conclusions**

Highly dispersive SrCO₃ nanostructures with unique ellipsoid, dumbbell, and rod-like morphologies were successfully synthesized by a facile way in pure methanol or methanol/water solution without additives. The morphology of SrCO₃ nanostructures can be controlled flexibly by adjusting the reaction temperature and the m/w ratio. N₂ adsorption-desorption result reveals that this dumbbell-like SrCO₃ has a mesoporous structure. It is expected that these SrCO₃ nanostructures can be used in photocatalysis and electronic manufacturing in the future.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

LL carried out the experiments studied on the crystal morphology, participated in the sequence alignment, and drafted the manuscript. Dr. RL designed the research programs and guided the experiment’s progress. Professors QF and ZT participated in the sequence alignment. All authors read and approved the final manuscript.
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