Facile synthesis of ultrafine and high purity spherical strontium carbonate via gas-liquid reaction

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Abstract
In this work, a simple gas-liquid precipitation reaction was developed to fabricate spherical strontium carbonate (SrCO₃) particles using strontium hydroxide (Sr(OH)₂), carbon dioxide (CO₂) and ethylene diaminetetraacetic acid strontium salt (EDTA-Sr) as raw materials. The effects of the concentration of EDTA-Sr and Sr(OH)₂, airflow rate of CO₂ and reaction temperature on the morphology of SrCO₃ were investigated. The results showed that spherical SrCO₃ particles can be formed when the concentration of EDTA-Sr reached 0.02 M as well as that of Sr(OH)₂ was less than 0.1 M. The airflow rate of CO₂ gas had little effect on the spherical morphology, and SrCO₃ microsphere with good dispersion could be obtained when the reaction temperature reached 50 °C. Under the optimal conditions ([EDTA-Sr] = 0.02 M, [Sr(OH)₂] = 0.1 M, 50 °C, [CO₂] = 11 l min⁻¹), high purity spherical SrCO₃ particles with diameter of 200–800 nm can be easily obtained. Finally, the growth mechanism of spherical SrCO₃ has been preliminarily presented, which indicated that EDTA-Sr is an excellent structure-directing agent for forming spherical SrCO₃ particles. Our work offers an effective method for large-scale production of high purity spherical SrCO₃.

1. Introduction
Strontium carbonate (SrCO₃) is an important inorganic material and widely used in special glass, ferrite magnets, ceramics, fireworks, pigments, catalysis, chemical sensors and electronic components [1–3]. The application of SrCO₃ depends on many properties, including chemical purity, morphology, particle dispersion, surface, density and dispersity [6–9]. Morphology is the most important parameter, so the control of strontium carbonate morphology is becoming an important part of studying SrCO₃. Recent advances have revealed that SrCO₃ with different morphologies have been prepared; these morphologies include sphere, rod, ellipsoid, needle, flower, ribbon, wire, bundle and dumbbell [10–15]. Of these, spherical powders offer many advantages such as specific surface area, high dispersion, and flowing properties. Adding PTC electronic components and luminescent materials can improve performance. Thus, the synthesis of SrCO₃ particles with spherical morphology has attracted significant interest due to their novel properties and potential applications.

A variety of methods have been developed to fabricate spherical SrCO₃ particles. Du et al. [16] employed ionic liquid (1,1,3,3-tetramethylguanidinium lactate) as a solvent to synthesize SrCO₃ spheres with diameters ranging from 200 to 400 nm, using SrCl₂·6H₂O, NaOH and CO₂ as raw materials. To avoid costly ionic liquid solvents, Cao et al. [17] used surfactant cetyltrimethylammonium bromide (CTAB) as soft-template to prepare spherical SrCO₃ particles via the hydrothermal method. Other surfactants, such as poly-(styrene-alt-maleic acid) (PSMA) [18], sodium dodecyl sulfate (SDS), or Pluronic F127, were also successfully used to obtain SrCO₃ spheres through the precipitation reaction of Sr(NO₃)₂ or SrCl₂ with Na₂CO₃. However, the hydrothermal method requires surfactants as soft-template is generally toxic and expensive. Recently, Zhu et al. [19, 20] reported synthesis of SrCO₃ spheres by adding EDTA-2Na or EDTA-2Na and MgCl₂ instead of surfactants to the solution.
of SrCl$_2$ and Na$_2$CO$_3$ via the hydrothermal method (190°C for 12 h). Although this method introduced EDTA-2Na as new morphology-control agent, it still involved high temperatures and long reaction times. The drawback of the above methods is that by-products such as NaCl or NaNO$_3$ formed from the reaction lead to the impurity of SrCO$_3$ spheres. These methods require a tedious post-treatment process to remove these byproducts for high purity SrCO$_3$ spheres. Therefore, a new method should address the issue of by-products and large-scale synthesis of high-quality SrCO$_3$ spheres.

In this work, we proposed a facile, low-cost and efficient approach for the fabrication of ultrafine and high purity spherical SrCO$_3$. The spherical SrCO$_3$ can be obtained by a simple gas-liquid reaction using Sr(OH)$_2$ and CO$_2$ as reactants, and EDTA-Sr was introduced into the reaction as the morphology-controlling agent. The effects of the concentration of EDTA-Sr and Sr(OH)$_2$ airflow rate of CO$_2$ and reaction temperature on the morphology of SRCO$_3$ were investigated. High purity SrCO$_3$ was produced without any post-treatment.

2. Experimental section

2.1. Materials
Analytical grade EDTA-Sr and Sr(OH)$_2$ were purchased from Xining Hongjian Fine Chemicals Co. Ltd (Xining, China) and used without further purification. High purity CO$_2$ gas was purchased from Xining Xingwei Gas Co. Ltd (Xining, China).

2.2. Synthesis of ultrafine spherical strontium carbonate
The entire experimental process includes solution preparation, reaction, centrifugal washing and drying process. First, 0.05 mol Sr(OH)$_2$ and 0.005 mol EDTA-Sr were dissolved in distilled water under stirring to form a 500 ml solution; then, the solution was heated to 50°C. Carbon dioxide was then introduced into the above solution at a rate of 1 l min$^{-1}$ for about 10 min, and white precipitate products were formed. The final precipitate products were centrifuged, washed with hot distilled water three times, and dried in a vacuum oven at 100°C for 2 h. The effects of the concentration of EDTA-Sr and Sr(OH)$_2$, airflow rate of CO$_2$ and reaction temperature on the morphology of SRCO$_3$ were studied.

2.3. Characterization methods
The final crystalline products were identified by x-ray diffraction (XRD, X' Pert PRO, PanAnalytical, Netherlands) equipped with Cu $\alpha$ radiation ($\lambda = 1.54178$ Å). The morphology of the samples was examined by scanning electron microscopy (SEM, JSM-5610LV, Japan) and transmission electron microscopy (TEM, JEM2100, Japan). Chemical bonds in the molecules of the final products were determined by the Fourier transform infrared spectrum (FT-IR, NEXUS 670, Nicolet, USA). The size distribution of as-obtained SrCO$_3$ spheres was measured by the laser particle size analyzer (MASTERSIZER 2000, Malvern, UK).

3. Results and discussion

3.1. The effect of the concentration of EDTA-Sr
In order to investigate the influence of the concentration of EDTA-Sr on the morphology of SrCO$_3$ particles, six samples were synthesized under conditions of [Sr(OH)$_2$] = 0.1 M, [CO$_2$] = 11 min$^{-1}$, 50°C and different concentrations of EDTA-Sr (a) 0.001 M, (b) 0.0025 M, (c) 0.005 M, (d) 0.01 M, (e) 0.02 M and (f) 0.04 M. In figure 1(a), a small amount of the structure-directing agent (0.001 M) was added into the reaction system, and the as-obtained particles appeared as bundle-like aggregates consisting of many small SrCO$_3$ needles aligned radially toward both ends. This could indicate that a small amount of the agent does not obtain spherical morphology. Therefore, the concentration of the agent was further increased to 0.0025 M, 0.005 M and 0.01 M, and the morphology of as-synthesized particles was obviously changed (as shown in figures 1(b)–(d)). The particles were irregular spherical aggregates and were made of some small spherical SrCO$_3$ particles. As the amount of the agent increased, the size of aggregates became smaller, which proved that EDTA-Sr also could reduce the agglomeration between particles. When the concentration of the agent reached 0.02 M and 0.04 M, perfect spherical SrCO$_3$ particles with good dispersion were obtained (figures 1(e) and (f)). Versus the above-mentioned irregular spherical aggregates, the size and shape were more homogeneous. The diameters of the products are 200–800 nm, and the morphology of the particles remained spherical, and the size did not change when the concentration of morphological agent increased to 0.04 M. Thus, 0.02 M is a suitable concentration for the shape control agent.
3.2. The effect of the concentration of Sr(OH)$_2$

In order to investigate the influence of the concentration of Sr(OH)$_2$ on the morphology of SrCO$_3$ particles, five samples were synthesized under conditions of [EDTA-Sr] = 0.02 M, [CO$_2$] = 11 min$^{-1}$, 50 °C and different concentrations of Sr(OH)$_2$ ((a) 0.025 M, (b) 0.05 M, (c) 0.1 M, (d) 0.2 M and (e) 0.4 M). When the concentration of Sr(OH)$_2$ was less than or equal to 0.1 M (0.025 M, 0.05 M and 0.1 M), the as-synthesized particles appeared sphere-like with good dispersion (figures 2(a)–(c)); when the concentration of the reactant was more than 0.1 M (0.2 M and 0.4 M), the morphology of as-prepared particles showed irregular agglomeration morphology (figures 2(d) and (e)). There are two possible reasons for the irregular morphology when the concentration of Sr(OH)$_2$ reaches 0.2 M and 0.4 M: The amount of morphology agent is insufficient (the molar ratio of EDTA-Sr and Sr(OH)$_2$ is 1:10 and 1:20, respectively) or the Sr(OH)$_2$ did not dissolve completely at 50 °C at higher concentrations. Thus, a high concentration of the reactant of Sr(OH)$_2$ and low molar ratio of EDTA-Sr and Sr(OH)$_2$ could not produce a spherical morphology. Therefore, the optimal concentration of Sr(OH)$_2$ should be kept at 0.1 M.

3.3. The effect of CO$_2$ airflow rate

To investigate the influence of CO$_2$ airflow rate on the morphology of SrCO$_3$ particles, six samples were synthesized under conditions of [EDTA-Sr] = 0.02 M, [Sr(OH)$_2$] = 0.1 M, 50°C with different CO$_2$ airflow rates: (a) 11 min$^{-1}$, (b) 2.5 l min$^{-1}$, (c) 5 l min$^{-1}$, (d) 10 l min$^{-1}$ and (e) 15 l min$^{-1}$. The as-obtained SrCO$_3$ particles were spherical with different aeration rates of CO$_2$ (see figure 3), indicating that the airflow rate of CO$_2$...
had little effect on the morphology. The effects of the concentration of additives and Sr(OH)$_2$ were much greater than the airflow rate. Therefore, 11 min$^{-1}$ was selected as the airflow rate of CO$_2$.

### 3.4. The effect of the reaction temperature

In order to study the effect of reaction temperature on the morphology of SrCO$_3$, five samples were synthesized at different reaction temperatures (20 °C, 30 °C, 40 °C, 50 °C and 60 °C). Figures 4 and 5 show the SEM images of the five samples at a magnification of 5000 and 20,000 fold. At a reaction temperature of 20 °C, as-obtained SrCO$_3$ particles appeared as irregular aggregates with small spherical local morphology and very serious agglomeration (figures 4(a) and 5(a)). When the reaction temperature reaches 30 °C and 40 °C, the resulting strontium carbonate particles have only slight agglomeration (see figures 4(b) and (c), and 5(b) and (c)). At 50 °C and 60 °C, the agglomeration phenomenon disappeared, and spherical particles had good dispersion and relatively uniform spherical morphology. All of the morphology of as-obtained SrCO$_3$ particles at different reaction temperatures is spherical (figure 5), which indicates that the reaction temperature has little effect on the morphology of the as-synthesized particles under these reaction conditions, but there will be agglomeration phenomenon in the low reaction temperature (figure 4). Therefore, a reaction temperature of 50 °C is appropriate.
3.5. Crystallization of SrCO$_3$ in the optimal conditions

Figure 6 shows the XRD pattern (figure 6(a)), IR spectrum (figure 6(b)), size distribution curve (figure 6(c)), SEM (figures 6(d) and (e)) and TEM images (figure 6(f)) of the ultrafine spherical SrCO$_3$ synthesized from gas-liquid reaction under optimal conditions ([EDTA-Sr] = 0.02 M, [Sr(OH)$_2$] = 0.1 M, [CO$_2$] = 11 min$^{-1}$, 50 °C). The XRD patterns show that all diffraction peaks were readily indexed to the orthorhombic SrCO$_3$ (lattice constants: $a$ = 5.107 Å, $b$ = 8.414 Å and $c$ = 6.029 Å). This is consistent with the values in the standard card (JCPDS 05-0418). Furthermore, the sharp diffraction peaks and no other impurity peaks indicate the pure crystallization and phase of SrCO$_3$.

Figure 6(b) shows the IR spectrum of SrCO$_3$ in the fundamental region. The sharp absorption peaks at 702 cm$^{-1}$, 859 cm$^{-1}$, 1070 cm$^{-1}$ and 1470 cm$^{-1}$ correspond well to the four characteristic absorption peaks of carbonates [21]. The band at 3425 cm$^{-1}$ corresponds to the adsorbed water. According to the size distribution curve of the final products, the particle size is normally distributed with an average particle size of about 500 nm. The SEM and TEM images showed that spherical SrCO$_3$ particles with a relatively uniform morphology and narrow size distribution were obtained. Figures 6(d) and (e) show that the diameter of microspheres was 200–800 nm. The TEM image (figure 6(f)) clearly showed that the diameter of a single as-synthesized SrCO$_3$ microsphere is about 500 nm. The magnified part shows that the surface of the spheres looks rather rough.

Figure 5. SEM images (20,000 ×) of products prepared in the presence of EDTA-Sr (0.02 M), [Sr(OH)$_2$] = 0.1 M, [CO$_2$] = 11 min$^{-1}$ and different reaction temperatures: (a) 20 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C and (e) 60 °C.
3.6. The formation mechanism of SrCO₃ spheres with EDTA-Sr as the additives

Three reactions described in the following are believed to occur in the gas-liquid reaction process:

\[
\begin{align*}
\text{Sr(OH)}_2 & \rightarrow \text{Sr}^{2+} + 2\text{OH}^- \\
\text{CO}_2 + 2\text{OH}^- & \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \\
\text{Sr}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{SrCO}_3 \downarrow .
\end{align*}
\]

At 50 °C, Sr(OH)₂ dissolves in water to Sr²⁺ and OH⁻. The CO₂ gas can then react with the existing OH⁻ in the solution to form CO₃²⁻; finally, Sr²⁺ reacts with CO₃²⁻ in the presence of EDTA-Sr to form spherical SrCO₃. EDTA-Sr plays an important role in the formation of SrCO₃ microspheres during the gas-liquid process. EDTA-Sr is a relatively stable coordinate compound with a relatively large conditional stability constant under alkaline conditions. As a structure-directing agent, it affects the morphology of SrCO₃ in two aspects. First, the agent adsorbed and limited Sr²⁺ within the symmetrical regions and further inhibited the crystal growth rate, leading to good dispersion of crystal growth of SrCO₃. Second, the additives absorbed on the different planes of SrCO₃ seeds, resulting in the same growth rate of different planes to form spherical SrCO₃ when the concentration of additives reached a critical value. Thus, by using EDTA-Sr as a modifier, spherical SrCO₃ particles are easily obtained through the absorption of EDTA-Sr.

The concentration control condition experiment indicates that the critical value of additives is determined when the molar ratio of EDTA-Sr and Sr(OH)₂ reaches 1:5. Moreover, in addition to the irreplaceable effect of EDTA-Sr, the reaction temperature also played an important role in the formation of the spherical SrCO₃ particles with good dispersion, as confirmed by the reaction temperature control experiments. In contrast with previous reports [19, 20], this work provided an easier gas-liquid reaction route to produce SrCO₃ spheres.

4. Conclusions

In summary, we successfully developed a facile gas-liquid reaction to synthesize spherical SrCO₃ particles using Sr(OH)₂, CO₂ gas and EDTA-Sr as reagents. The influence of the concentration of EDTA-Sr and Sr(OH)₂, airflow rate of CO₂ and reaction temperature on the morphology of SrCO₃ were well studied. It was found that spherical SrCO₃ particles can be formed when the concentration of EDTA-Sr reached 0.02 M and Sr(OH)₂ was less than 0.1 M. The airflow rate of CO₂ gas had little effect on the spherical morphology. When the reaction temperature reached 50 °C, spherical SrCO₃ with good dispersion can be prepared. Furthermore, high purity spherical SrCO₃ particles with diameter of 200–800 nm can be easily obtained under optimal conditions ([EDTA-Sr] = 0.02 M, [Sr(OH)₂] = 0.1 M, 50°C, [CO₂] = 11 min⁻¹). In addition, a simple adsorption mechanism has been proposed to explain the formation of SrCO₃ microspheres, which demonstrated that EDTA-Sr plays an important role in controlling the morphology of spherical SrCO₃ particles.

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Conflicts of interest

There are no conflicts to declare.

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