Nucleation Controlled in the Aggregative Growth of Strontium Carbonate Microcrystals

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Abstract The influence of PABA(p-aminobenzoic acid) and HEEDTA (N-(2-hydroxyethyl) ethylenediamine-N, N', N''-triacetic acid) on Strontionite crystals via simple CO2 diffus ion route is described. The results showed that the experimental parameters have great influence on the shape evolution of products. The presence of templating species and varied pH are the key primary conditions for the growth morphology. Spike like crystals self assembled in the form of flower like and cauliﬂower shaped cluster with high crystallinity were identiﬁed. The crystals undergo an interesting morphology changes and have been characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) techniques.

Keywords Biomaterials, Composite Materials, Crystal Growth, Electron Microscopy, p-amino Benzoic Acid, N-(2hydroxyethyl) Ethylenediamine-N, N', N''- Triacetic Acid

1. Introduction

The ability to manipulate the morphogenesis of materials through chemical synthesis is an important requirement of modern materials[1] chemistry, due to the fact that shape, dimension, and size of materials have great influence on their physico-chemical properties and their related applications. Among the variety of morphologies, self-assembled structures have been extensively studied due to their potential applications in various nanodevices[2,3]. However, only a few groups have examined synthetic methods that lead to assembled SrCO3 structures. Literature reports shows that, surfactants or templates, need to be disposed for obtaining pure sample[4,5]. Therefore, it is still a challenge to develop simple and reliable synthetic methods for the synthesis of self-assembled structures.

Strontium carbonate (SrCO3) is widely used starting material of strontium for preparing a variety of strontium compounds,[6-8]. This has two traditional main applications. An additive in the production of glass for color televis ion tubes and constituent of ferrite magnets[9,10]. In recent years, researchers have found additional applications of SrCO3 in other ﬁelds. Zhang and co-workers[11] discovered nanosized SrCO3-based chemiluminescence sensor showing high selectivity to ethanol and no response to foreign substances, such as gasoline,ammonia and hydrogen. Sreedhar et al synthesized SrCO3 hierarchical structure by natural materials[12] and organic additives[13]. Different SrCO3 hierarchical structures, such as flower -like[14], bundle-like, dumbbell-like, hexagonal star-like[15, 16], branch-like[17], especially spherical or sphere-like[14-16, 18] rods, whiskers and ellipsoids,[19] fibers,[20] have been prepared using different methods, including reverse micelles,[21] solvothermal methods[22] liquid-liquid interfaces[23]. Though the methods are encouraging there is considerable scope for further study to improve the quality. SrCO3 microstructures, have attracted extraordinary attention due to their novel applications as sensors having chemiluminescence[24], catalyst[25, 26], color television tubes, chief constituent of ferrite magnets[27].

We are reporting the successful synthesis of SrCO3 structures of spike like and cauliﬂower shaped morphology, efficiently achieved by using two organic additives– PABA and HEEDTA with simple CO2 gas f l ow diffus ion technique.

2. Experimental

2.1. Materials

Para-aminobenzoic acid(C7H7O2N),N-(2hydroxyethyl) ethylenediamine-N,N',N''-triacetic acid (C10H18O7N2), Ammonium carbonate (NH4)2CO3, sodium hydroxide (NaOH) and strontium chloride (SrCl2) were of analytical grade and used without further puriﬁcation. Double distilled water was used in all experiments.
2.2. Characterization

X-ray diffraction measurements of the strontium carbonate hierarchial structures were recorded using a Rigaku diffractometer (Cu radiation, λ = 0.1546 nm) running at 40 kV and 40 mA (Tokyo, Japan). FT-IR spectra of SrCO₃ structures were recorded with a Thermo Nicolet Nexus (Washington, USA) 670 spectrophotometer. Crystals were collected on a round cover glass (1.2 cm), washed with deionized water and dried in a desiccator at room temperature. The cover glass was then mounted on a SEM stub and coated with gold for SEM analysis.

2.3. Preparation of SrCO₃ Microcrystals

A typical procedure for preparation of crystalline SrCO₃ crystals was carried out as follows: In a glass bottle 2.5 mmol SrCl₂, 0.1 mmol PABA/HEEDTA were dissolved in 20 mL water and was stirred continuously to ensure complete solubility. Then the pH of the solution was adjusted to 7.0 and 10.0 by using 0.1M NaOH. After that the prepared solution was then covered with parafilm which was punched with three needle holes and placed in larger desiccator containing freshly crushed ammonium carbonate (20 g) at the bottom. After 24hr crystallization, the parafilm was removed and the white precipitate deposited on the glass bottle centrifuged and washed thoroughly with distilled water, followed by ethanol and allowed to dry at room temperature for further crystallization.
3. Results and Discussion

3.1. Effect of Additives on the Morphology of SrCO₃

Significant changes in the morphologies were observed when the pH of the reaction conditions varied between 7 and 10. Figure 1 and 2 shows the SEM images of SrCO₃ structures by adding the additives PABA and HEEDTA at different pH conditions. In general SrCO₃ dendrimers are obtained in the absence of additive[12], while in the presence of PABA at initial pH 3.0, individual spike like crystals were observed (Figure 1a, b). When the pH of the reaction mixture was increased to 7, the individual spikes aggregates to coniform like structures (Figure 1c, d). On further increasing the pH to 10.0, the spikes aggregates more closely and self assembled into flower like structures (Figure 1e, f). Figure 2a shows the SEM images of SrCO₃ structures in the presence of the additive HEEDTA. Remarkable changes in the morphology was observed with this additive and the shape of SrCO₃ structures changed from dendrimeric to cauliflower bunch like structures with short spikes of subunits having smooth surface at initial pH 3 (Figure 2a, b). At neutral pH mixed phase of cauliflower bunches with rough surface and spadix shaped structures with fibre like units are identified (Figure 2c, d). At pH 10.0, morphology of the SrCO₃ structures appears similar to that observed at pH 3 with rough surface (Figure 2c, d). The strontianite crystals clearly aggregates into cauliflower bunch like and coniform structures in CO₂ diffusion route. To the best of our knowledge, such close packed aggregates of strontianite crystals have not been observed in other biomimetic approaches to the growth of SrCO₃ crystals.

3.2. Structural Characterization of SrCO₃ Microcrystals

The XRD pattern of the isolated solids could be indexed to that orthorhombic structure of strontium carbonate and all the peaks are assigned by using JCPDS (05-418). The results implied that the aggregation did not alter the phase structure of SrCO₃. To our expectation, the crystallinity nature of the product was sensitive to that pH conditions. At lower pH condition showed a greater crystallinity than the product prepared under higher pH condition, implying the influence of solution pH on the crystallinity. In Figure 3 the pattern of SrCO₃ crystals obtained in aqueous solution displays the following diffraction peaks with (hkl) indices (110), (111), (021), (002), (121), (200), (130), (220), (040), (032), (041), (202), (132), (141) respectively. Similarly in figure 4, the diffraction peaks with (hkl) indices (110), (111), (021), (002), (121), (200), (112), (220), (032), (040), (132), and (113), of pure orthorhombic strontianite respectively. It may also be seen that the peak (111) is the strongest, suggesting that SrCO₃ crystals obtained in aqueous solution grow mainly along with the (111) phase.

3.3. FTIR Studies

To identify the growth mechanism and the effect of PABA and HEEDTA on SrCO₃ microstructures, the sample was analyzed by FT-IR spectroscopy. The sharp peaks at 856, 703 cm⁻¹ (Figure 5a), 855, 701 cm⁻¹ (Figure 5b) and 857, 701 cm⁻¹ (Figure 5c) are in-plane and out-plane bending of CO₃²⁻.
The IR bands at 1476, 1469 and 1465 cm\(^{-1}\) (Figure 5a, b, c) correspond to the asymmetric stretching mode of C-O bond while the weak band at 1074 cm\(^{-1}\) (Figure 5b, c) is attributed to the symmetric C-O stretching vibration. The band at 3418 cm\(^{-1}\) (Figure 5b) can be attributed to OH stretching vibration due to hydrogen bonding and or N-H stretch of the –NH\(_2\) group from the functional groups present in additives. The band at 3423 cm\(^{-1}\) (Figure 5c) can be attributed to OH stretching vibration due to hydrogen bonding and or N-H stretch of the –NH\(_2\) group from the functional groups present in additive.

In comparison with Figures 5b, the C-O stretching vibration peak around 1465 cm\(^{-1}\) in Figure 5c, shifts to higher frequency by 4 cm\(^{-1}\) (1469 cm\(^{-1}\)), suggesting that PABA and HEEDTA have different influence of SrCO\(_3\). This is probably due to the fact that the two organic molecules can adsorb onto the different planes of SrCO\(_3\) nuclei and influence the mode of crystal growth, resulting in little change of microstructure.

### 4. Conclusions

In summary, uniform hierarchical SrCO\(_3\) complex structures in the form of spike like and cauliflower bunch like units were efficiently obtained by a facile ammonium carbonate method in the presence of PABA and HEEDTA as additives. The present uniform hierarchical SrCO\(_3\) structures were self assembled by the related crystalline particles, assisted by the additives would enlarge the potential applications of strontium carbonate microstructures. This strategy may also be expected for the preparation of other metal carbonates.

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