

Bubble-assisted Assembly of Nanocrystals into Hierarchical Structures

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Alkaline-earth carbonates (M = Ca, Sr, and Ba) with delicate hierarchical structures were prepared via self-assembly of nanocrystals in solution without using any surfactant at room temperature. The CO₂ generated during the coprecipitation is believed to play an important role in the formation of these structures.

Recently, assembling nanoscale building blocks into hierarchical structures have received much attention since morphology and size play very important roles in determining chemical and physical properties of materials.^{1,2} A large number of complex functional architectures consisting of 1D nanoscale building units have been fabricated by various methods.^{3–5} A common synthetic approach is based on solution-phase growth in the presence of surfactant, which can form diverse assembly in solution and be used as template. The formation of a hierarchical structure always involves a series of complicated processes, including chemical reaction, nucleation, and growth, which are affected by many factors, such as concentration, growth modifiers, and interparticle interactions. The complexity of these processes makes it difficult to understand the exact role of individual experimental parameters. Simplification of assembly processes would be more favorable for understanding the formation of hierarchical structures from nanoscale components. In this letter, we demonstrate a very simple, surfactant-free approach to assemble MCO₃ (M = Ca, Sr, or Ba) nanocrystals into hierarchical structures in solution at room temperature. Herein, the carbonate was chosen as a model system because it is an important biomineral in nature and has been widely studied for biocrystallization.

In a typical procedure for preparing carbonate with hierarchical structure, 100 mL of M(NO₃)₂ (0.24 M) was added to 100 mL of NH₄HCO₃ solution of the same concentration with the above solution under vigorous stirring at room temperature. After the mixed solution was stirred for about 30 min, the precipitate was collected by filtration, washed several times with deionized water, and dried at room temperature for 24 h. The phase of the product was identified using an X-ray diffractometer (XRD, X'Pert, PANalytic, the Netherlands) with CuK α radiation (40 kV, 30 mA). The size and the morphology of the product were characterized with a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) and a transmission electron microscope (TEM, H-700, Hitachi, Japan).

Figure 1 displays the XRD patterns of the as-prepared carbonate powder. The diffraction peaks of SrCO₃ and BaCO₃ can be perfectly indexed to a pure orthorhombic phase, and no other impurities were detected in the two samples. In the case of the CaCO₃, the diffraction peaks corresponding to calcite and vaterite were observed. It is well known that CaCO₃ exists in three crystal structures, i.e., calcite, aragonite, and vaterite. The

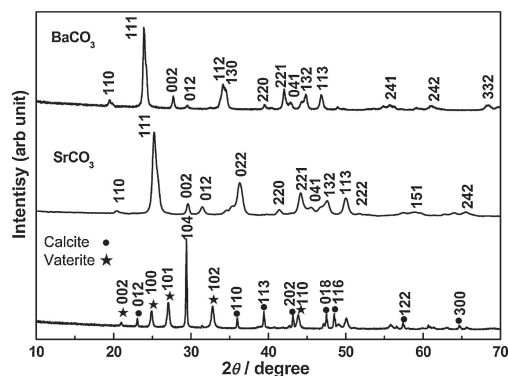


Figure 1. XRD patterns of the as-prepared carbonates.

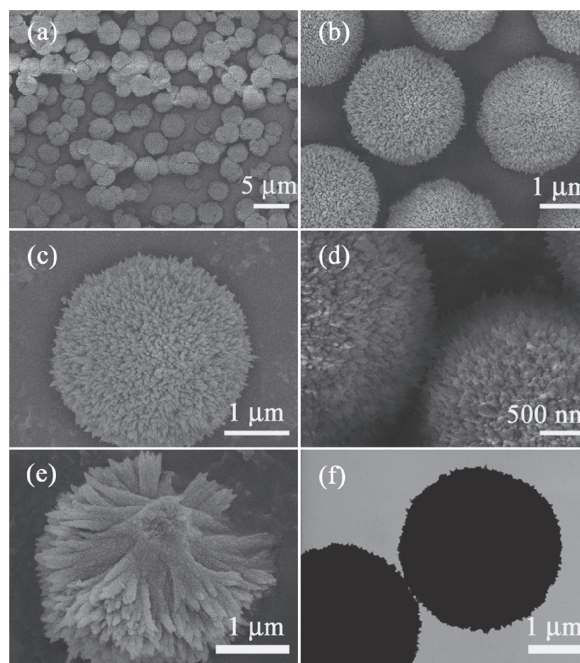


Figure 2. (a–d) SEM images of SrCO₃ microspheres observed under different magnifications; (e) SEM image of a fragmented half of a microsphere; (f) TEM image of SrCO₃ particles.

phase of CaCO₃ obtained by coprecipitation is sensitive to the experimental conditions, especially the pH in the precursor solution.⁶

Figure 2 shows SEM and TEM images of the as-prepared SrCO₃ particles. As shown in Figure 2a, the low-magnification image indicates a high yield of SrCO₃ microspheres. The higher magnification images (Figures 2b–2d) demonstrate that the microsphere had rough surface structures and that many macro-

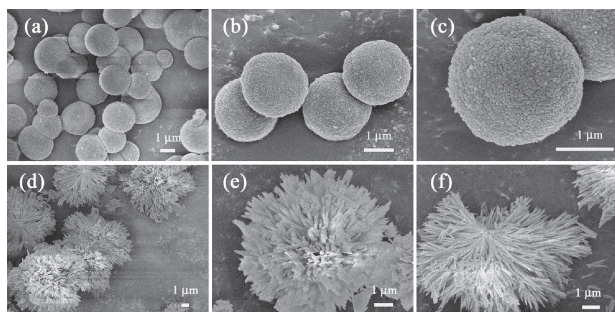
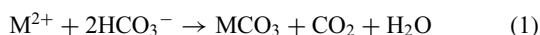


Figure 3. SEM images of the as-prepared (a–c) CaCO_3 and (d–f) BaCO_3 .

pores existed on the surface. Further SEM observation of the fragmented half of a microsphere reveals that the SrCO_3 microsphere was in fact made up of many nanoneedles originating from the same core (Figure 2e), and a regular separation between single nanoneedles was observed. In agreement with the above SEM findings, high geometric symmetry of the examined microsphere can be seen from the TEM image (Figure 2f). SEM images of the CaCO_3 and BaCO_3 are shown in Figure 3. It can be seen that the CaCO_3 product consisted of microspheres, which were in close contact with each other (Figures 3a and 3b). Close examination (Figure 3c) showed that the microsphere was made up of nanoparticles. The as-prepared BaCO_3 also exhibited interesting hierarchical structure. As shown in Figures 3d–3f, the BaCO_3 particles were mainly of flower-like nanodendrite bunches.

The influence of synthesis conditions on morphology development was experimentally investigated. The results revealed the source of M^{2+} had no obvious effect on the morphology and structure of the final product. However, when the NH_4HCO_3 was replaced by $(\text{NH}_4)_2\text{CO}_3$ or Na_2CO_3 , the final products were large particles with irregular shape. In the present work, the major chemical reaction for the formation of carbonate in the aqueous solution can be formulated as



When the HCO_3^- was replaced by CO_3^{2-} , no CO_2 was released during the growth of the MCO_3 crystal. Therefore, it can be concluded that the formation of the hierarchical structures should be greatly related to the released CO_2 .

To understand the formation of the hierarchical structures, the products collected at different precipitation time were analyzed by SEM. Herein, we chose SrCO_3 as the model because it has only one polymorph and more complex morphology. As shown in Figure 4, a time-dependent self-assembly and growth of “nanocrystal-to-rod-to-dumbbell-to-sphere” evolution was observed. Since no templates or surfactants were used, it is reasonable to assume that the formation of hierarchical SrCO_3 microspheres is governed by oriented attachment because the mineralization is mainly driven by interaction of the particles rather than by the organic ligand.⁷ Based on the above experiments, a possible mechanism involving bubble-assisted assembly can be speculated. The addition of Sr^{2+} -containing solution to the HCO_3^- solution produced large amounts of SrCO_3 nuclei in solution according to reaction 1. At the same time, CO_2 was generated and may serve

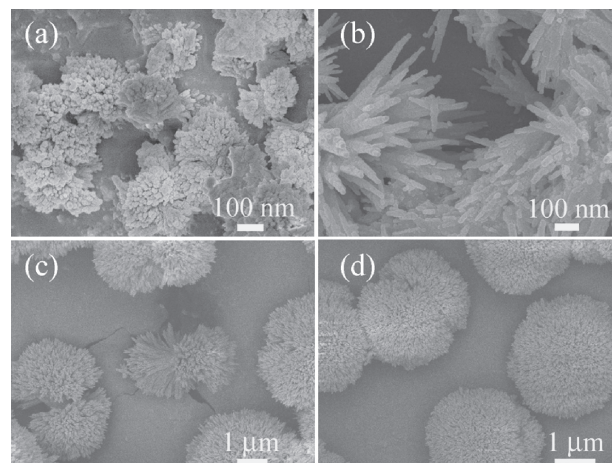


Figure 4. SEM images of intermediate SrCO_3 products obtained at different precipitation time: (a) 1, (b) 3, (c) 15, and (d) 20 min.

as the aggregation center, on which the particles further grew or attached, leading to formation of the hierarchical structure. Note that the variation of morphology and size of MCO_3 with the M^{2+} may be related to the nature of the carbonate. Further study is still needed to clarify the exact growth mechanism for formation of the different hierarchical structures.

In summary, we demonstrated a very simple process for assembly of carbonate nanocrystals into hierarchical structures. The CO_2 generated during precipitation is believed to play an important role in formation of the structures. The gas-assisted assembly mechanism would be helpful for understanding other nanofabrication processes. Furthermore, the method may be extended to other materials with hierarchical structures for specific applications.

References and Notes

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