Evolution of Calcite Nanocrystals through Oriented Attachment and Fragmentation: Multistep Pathway Involving Bottom-Up and Break-Down Stages

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Supporting Information

ABSTRACT: A nonclassical multistep pathway involving bottom-up and break-down stages for the evolution of calcite nanograins ∼50 nm in size was demonstrated in a basic aqueous system. Calcite nanofibrils ∼10 nm wide were produced as the initial crystalline phase via amorphous calcium carbonate through ion-by-ion assembly by the carbonation of Ca(OH)2 at a high pH of ∼13. Bundles ∼50 nm in diameter were then formed by the subsequent oriented attachment of the nanofibrils. Monodispersed calcite nanograins were finally obtained through spontaneous fragmentation of the fibrous forms via a decrease in pH by further carbonation.

INTRODUCTION

Monodispersed nanocrystals have attracted much attention because of their specific properties originating from a high specific surface area, high dispersivity, and quantum size effects.¹⁻⁶ Nanometer-scale crystals of metal oxides and sulfides are utilized as phosphors, catalysts, photocatalysts, fillers, and raw materials for sintered ceramics. In general, miniaturization of crystalline grains to the nanometer scale is achieved by either a break-down or bottom-up process. The size and shape of the resultant grains are not strictly controlled by break-down routes, such as the grinding and milling of large crystals. Uniform nanometer-scale grains are commonly synthesized via homogeneous nucleation and subsequent growth as a bottom-up route through the accumulation of ions or molecules as illustrated in Figure 1a.⁷⁻¹⁴ The grain size and distribution are adjusted on a nanoscale by changing the frequency of nucleation and the inhibition of growth by adding modifying agents. In the present article, we report a multistep formation process of nanoscale crystalline grains through ion-by-ion accumulation to fibrils and their oriented attachment in the bottom-up stage and subsequent fragmentation in the break-down stage, as illustrated in Figure 1b. Monodispersed nanograins are produced via a nonclassical complex pathway including bottom-up and spontaneous break-down stages. Calcium carbonate is an important material in various industrial fields. Specifically, calcite particles are commonly used as fillers for papers, rubbers, plastics, and paints. The size variation of calcite particles at the nanometer scale is essential to control the optical and mechanical properties of host materials.¹⁵,¹⁶ Wet chemical processes using aqueous systems are applied for the fabrication of nanometer-scale calcite particles. The shape and size of calcite crystals are varied by conditioning the reaction time, solute concentrations, temperature, and the addition of modifying agents.¹⁷,¹⁸ Monodispersed calcite nanocrystals are conventionally produced

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Figure 1. Schematic illustrations of a classical pathway (a) and nonclassical multistep pathway involving bottom-up and break-down stages (b) for the evolution of nanograins from ions.
without modifying agents by the carbonation of a calcium hydroxide (Ca(OH)$_2$) aqueous dispersion as an industrial process.$^{18,19}$ The control parameters have been established for industrial fabrication of stably dispersed calcite nanocrystals without modifying agents. However, the evolution mechanisms of calcite nanocrystals without modifying agents have not been clarified sufficiently in the conventional aqueous systems. Thus, we monitored the evolution of calcite nanocrystals carefully and then found that the nanocrystals were formed through a nonconventional route.

Calcite is regarded as a major crystalline phase of biominerals, such as seashells$^{20,21}$ eggshells$^{22,23}$ and the skeletons of sea urchins$^{24,25}$ and foraminifera$^{26-28}$ In recent years, it has been shown that specific hierarchical architectures in various calcite-based biominerals exhibit mesoscopic granular textures consisting of nanocrystals 10−100 nm in size.$^{29,30}$ The subunits of calcite nanocrystals are arranged in the same crystallographic direction in the body of biominerals. Specific properties of the biominerals are ascribed to ordered architectures formed by the oriented nanocrystals. Nonclassical pathways, such as the presence of amorphous intermediates and oriented attachment of unit grains, have been proposed for the production of specific hierarchical architectures.$^{24,25,31,32}$ In previous works, organic molecules were reported to promote the nonclassical crystallization routes. Hence, biomimetic and bioinspired mineralization through amorphous calcium carbonate (ACC) and oriented attachment has been studied using aqueous systems including organic modifiers.$^{33,34}$ However, we showed that the presence of organic molecules is not essential on the nonclassical pathway for the crystallization of calcium carbonate.$^{35-37}$ Further investigation of the evolution of calcite crystals on a nanometer scale without organic species is still important to understand the nature of calcium carbonate.

In the present work, we monitored changes in the morphology of calcite nanocrystals produced by the carbonation of Ca(OH)$_2$ suspension. The results show a nonclassical multistep pathway for the evolution of monodispersed calcite nanograins including ion-by-ion accumulation, particle-by-particle assembly, and spontaneous fragmentation. Our findings reveal the specific nature of calcium carbonate on crystallization. Moreover, this is the first report on a nonclassical complex route for the evolution of uniform nanometer-scale grains via both bottom-up and break-down stages.

## EXPERIMENTAL SECTION

We studied the evolution of calcite nanocrystals in the procedure reported in our previous article.$^{35}$ Detailed procedures were described in the Supporting Information. Calcite crystals were synthesized in a 200 cm$^3$ aqueous dispersion of 42.5 g dm$^{-3}$ Ca(OH)$_2$ (Figure S1) through carbonation by the introduction of CO$_2$ at a rate of 3.0 dm$^3$ min$^{-1}$. The formation of calcite nanocrystals in the aqueous system was monitored with the variation of pH by carbonation. The system was neutralized by the introduction of CO$_2$. The evolution of calcium compounds was divided into five steps as shown in Figures 2 and 3 on the basis of the pH variation and the reaction mode monitored by transmission electron microscopy (TEM, FEI Tecnai F20, operated at 200 kV) with selected area electron diffraction (SAED). The dispersion was dropped on a copper grid covered with a collodion film for TEM observation of the products.

![Figure 2. pH-transitive graph of the Ca(OH)$_2$ dispersion by the introduction of CO$_2$ (a); Raman scattering spectra (b) and X-ray diffraction (XRD) signals (c) for powdery samples obtained in the reaction steps. ICDD: 00-044-1481 (Ca(OH)$_2$), 00-005-0386 (calcite).](https://doi.org/10.1021/acsomega.7b01487)
methods. We rearranged several TEM images of nano fibrils in step 2 and step 3 to clarify the oriented attachment in the Supporting Information (Figure S3). According to spots in the SAED pattern (Figure 3c), the bundles of several fibrils exhibited a single crystalline feature. The TEM images and the SAED pattern suggest that the bundles of calcite were produced through the oriented attachment of nano fibrils elongated in the c direction.

In step 4 (RP: 15−20 min (Figure 2a)), rugged surfaces were formed with the fusion of nano fibrils in the bundles with a decrease in pH (Figure 3d). When the pH of the dispersion decreased to ~7, we observed infinite nanograins ~50 nm in size. Finally, monodispersed nanocrystals were obtained after the neutralization in step 5 (Figures 3e1 and S4). Rhombohedral grains were unifaceted, with {104} faces (Figure 3e2).

As mentioned above, calcite nanograins were produced in the basic solution system through a nonclassical pathway divided into five steps involving bottom-up and subsequent break-down stages. Step 1 is the formation process of a metastable amorphous phase as a precursor of the stable crystalline phase. Step 2 is a classical growth pathway to crystal formation involving nucleation and growth with dissolution of the precursor. Step 3 is a bundling process by the oriented attachment of subunits regarded as a nonclassical growth route. Step 4 is a fragmentation process as a spontaneous break-down stage to form nanograins.

Spherical ACC particles were observed in step 1 (Figure 3a). The metastable amorphous phase is usually formed under a high supersaturated condition. A large amount of calcium ions supplied by the dissolution of Ca(OH)2 is rapidly reacted with CO3\(^{2−}\) by the introduction of CO2 in the basic dispersion. The amorphous phase is usually stabilized in the presence of organic agents.41,42 Here, in the present system, ACC without organic molecules would enter crystalline phases easily.

As shown in Figure 2a, ACC and calcite fibrils coexisted in step 2 (RP: 5−10 min) and the first half of step 3 (RP: 10−13 min). Thus, the transformation of the amorphous phase to calcite occurred in those stages (RP: 5−13 min). In the initial step 2, the nucleation of calcite nanocrystals was observed on the surface of ACC spheres, not inside the precursor (Figure 3b). Moreover, the elongation of calcite occurs on the outside of ACC. These facts indicate that calcite fibrils are formed from the nuclei via the accumulation of Ca\(^{2+}\) and CO3\(^{2−}\) ions supplied by dissolution of ACC. It means that the dissolution−deposition process was dominant for the formation of calcite fibrils rather than solid-state transition in the present study. In previous works, the amorphous phase stabilized by organic molecules was reported to change calcite directly.43,44 In the current system, however, ACC without organic agents is rapidly dissolved in the aqueous system. The growth of calcite fibrils was then observed on the surface of ACC by the deposition of supersaturated ions. Rhombohedral shapes are usually formed with the stable {104} faces of calcite. However, the crystal body is elongated in the c direction under basic conditions (Figure 4a). The growth of faces parallel to the c-axis of calcite is inferred to be inhibited by OH\(^{−}\) in this system. Figure 4c shows the ion positions of the (100) and (001) faces of calcite. Anionic and cationic planes in the calcite lattice are alternatively stacked in the c direction. The OH\(^{−}\) ions on the (001) planes are deduced to be easily replaced by CO3\(^{2−}\) ions because of a
large difference of their ion sizes. Thus, Ca\(^{2+}\) ions are provided immediately to the CO\(_3^{2-}\) ions. Calcite is then elongated in the c direction via ion-by-ion accumulation as the initial step in the bottom-up stage.

In step 3, calcite nanofibrils are bundled through oriented attachment (Figure 4a). Further carbonation replaces OH\(^-\) with CO\(_3^{2-}\) on the side faces of fibrils with a slight decrease in pH. The presence of Ca\(^{2+}\) ions promotes side-by-side attachment of the carbonated fibrils. Thus, bundled rods are formed through particle-by-particle accumulation as the second step in the bottom-up stage to reduce the total surface energy. Here, the crystallographic direction of the fibrils is inferred to be aligned in the same orientation.

In step 4, spontaneous fragmentation of calcite bundles occurs as the break-down stage after fusion of the fibrils with a drop in pH (Figure 4b). Partial dissolution—redeposition is enhanced around the calcite bundles by increasing the solubility of calcite crystals with neutralization. The fragmentation of nanorods is induced by increasing the solubility with decreasing pH. Thus, the chemical components of acid for neutralization are not essential for fragmentation. The grain boundary in the bundles would disappear with the reconstruction. The fragmentation is caused by the formation of the most stable \{104\} faces on the side of bundles. The stable faces are enlarged under the neutral condition. On the other hand, we obtained calcite nanofibers before fragmentation from the basic dispersion at pH \(\approx 12\) in step 4.\(^{35}\)

In step 5, monodispersed nanograins are finally produced by the fragmentation of bundles in a neutral system (Figure 4b). Rhombohedral grains are unifaceted with the most stable \{104\} faces (Figure 4b). Moreover, calcite nanograins are stably dispersed because their surface is positively charged outside of the isoelectric point (pH 11.5).

The essence of multistep evolution of calcite nanocrystals is a change in the growth mode with the variation of pH by carbonation. A high degree of supersaturation in the initial step (step 1) is buffered by the formation of the amorphous phase. The nucleation of calcite occurs with dissolution of the amorphous phase, and subsequent preferential growth in the c direction is then induced at a high pH of \(\sim 13\) (step 2). A slight decrease in pH reduces the repulsion force on the side face of fibrous forms elongated on the c-axis and promotes their oriented attachment (step 3). A drop in pH enhances the morphological change with the formation of stable faces of calcite. Finally, nanograins covered with the stable faces are formed with the neutralization (step 4). The change in growth mode from the bottom-up stage to the break-down stage is ascribed to the pH variation. The formation of calcite rods and granular textures in foraminifera shells was reported to be induced under a high pH condition.\(^{65}\) Our finding of various growth modes of calcite depending on the pH would be useful for understanding the formation mechanism of these fascinating biogenic architectures.

**CONCLUSIONS**

We reported a nonclassical complex pathway for nanocrystal formation via bottom-up and break-down stages through an amorphous phase. The evolution of calcite nanocrystals from Ca(OH)\(_2\) was demonstrated via the carbonation of a basic aqueous system. Monodispersed calcite nanograins \(\sim 50\) nm in diameter were produced through the formation of nanofibrils \(\sim 10\) nm wide and the subsequent oriented attachment of fibrils to bundles \(\sim 50\) nm wide (bottom-up stage) and spontaneous fragmentation of the fibers (break-down stage). These results show the specific nature of calcium carbonate, which is an important material not only for industrial applications but also in biogenic fields, with regard to the evolution of the crystal phase and morphology in aqueous systems.
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