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Self-organized formation of a hierarchical self-similar structure with calcium carbonate

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Self-organized growth of calcite crystals in a supersaturated solution with a gradual increase in the influence of silicate anions resulted in the formation of a hierarchical self-similar morphology consisting of three-pointed stars with sizes ranging from 100 nm to 100 μm.

Hierarchical unique morphologies ranging over nano- to macroscale length are essentially responsible for the appearance of biominerals produced by various kinds of life. However, details of the formation mechanism for the non-crystallographic complex shapes have not been clarified. Although crystallographic habits and appearances are well known to be modified by the selective adsorption of organic molecules or ionic species on specific crystal surfaces,[1–8] the variation is limited within the crystallographic symmetry. Recently, the formation of crystals showing unusual morphologies has been reported in inorganic systems containing polymer additives and surface-activating reagents.[9–11] García-Ruiz *et al.*[12–16] showed that carbonate crystals produced by the reaction of an alkaline-earth cation and a carbonate anion in silica gel exhibited unusual and unique shapes consisting of small crystals. These facts suggest that inorganic crystals having biomineral-like morphologies could be formed without organisms. Clarification of the morphological formation through self-organization would provide new information for unique morphogenesis in non-equilibrium systems including biomineralization processes. Moreover, understanding the formation mechanism of the remarkable architecture should develop chemistry for manufacturing micron- and nanoscale functional materials in solution systems. In this letter, we report that a regular rhombohedron of calcite was transformed into a self-similar structure consisting of three-pointed stars with specific adsorption of silicate anions. This new type of morphology of calcite is formed though self-organization induced by a gradual increase in the influence of the impurity.

A rhombohedron consisting of the basal {10–14} planes, which is the thermodynamically stable shape of calcite-type calcium carbonate, was commonly produced by direct mixing of a calcium chloride solution and a sodium carbonate solution. The regular forms of the rhombohedron and its hopper growth were also found by mixing the cations and anions in silica gel at a pH ranging between 7 and 10.† On the other hand, unusual porous morphologies having a threefold rotation symmetry (3m) were formed in silica gel at a pH of about 10 to 11 (Fig. 1a). This three-pointed star was confirmed to be calcite by X-ray diffraction. Similar calcite fibres having three ribs arranged with 3m symmetry have been reported by García-Ruiz *et al.*[14] In this study, we found many small, three-pointed stars 1 to 5 μm wide attached in the primary star (Fig. 1b). The secondary star-like units also consisted of smaller three-pointed stars 0.1 to 0.5 μm wide (Fig. 1c). The SEM observation indicates that this calcite having a hierarchical structure associated with a typical fractal figure 'Sierpinski gasket' was a single crystal because the star-like subunits were arranged with the same crystallographic orientation. In the early stage of the growth process of the hierarchical structures, regular rhombohedral shapes were formed, and then they were elongated along the c axis (Figs. 2a and b). This initial morphological change on calcite crystals is

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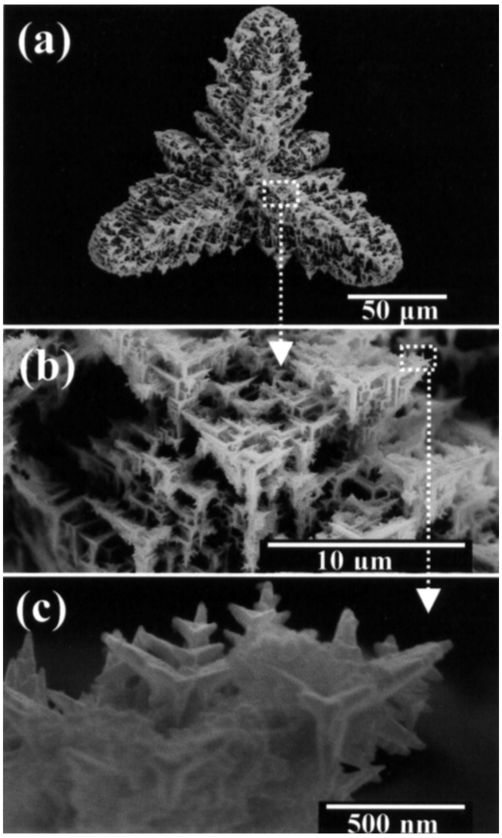

Fig. 1 Scanning electron micrographs of a calcite crystal showing threefold rotation symmetry grown in silica gel at pH 10.5 for 72 h.

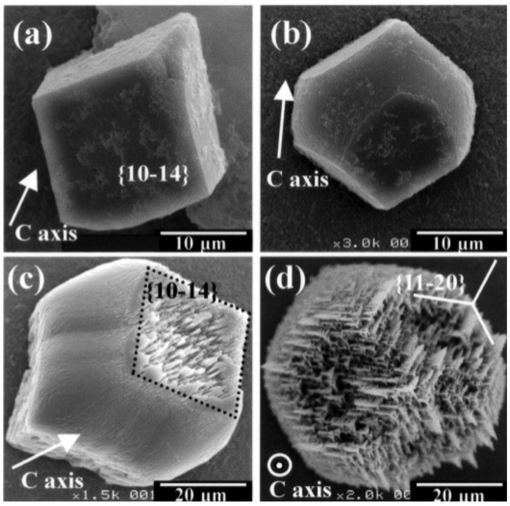

Fig. 2 Scanning electron micrographs of crystals grown in silica gel at pH 10.5 for 1 h (a), 3 h (b), 6 h (c) and 12 h (d).

similar to that induced by several organic molecules.[3] In this case, however, roughening on the {10–14} planes and subsequent growth of many small projections along to the c axis occurred in the progressive stage (Figs. 2c). The growing edges of the small projections on the basal crystal branched to three directions parallel to the {11–20} planes and perpendicular to the c axis (Figs. 2d). Finally, a hierarchical self-similar structure consisting of three-pointed stars with a three-fold rotation symmetry (Fig. 1) was achieved through the gradual evolution of growth behaviour.

Since the hierarchical structure was only produced in silica gel at high pH (above 10), the formation could not be attributed to the influence of the gel matrix or a high pH condition. García-Ruiz *et al.*[16] suggested that the change in crystal habit of calcite in silica gel was associated to the presence of silicate anions at the high pH. The solubility of silicate anions such as $SiO(OH)_3^-$ and $Si_4O_6(OH)_6^{2-}$ gradually increases above pH 9.[17] The soluble silicate anions of 10–100 mM at pH 10–11 influenced the morphology of the calcite crystals. We found the formation of single crystals having a self-similar morphology at a low carbonate concentration below 100 mM. In particular, a distinct shape of the morphology was obtained at the carbonate concentration of 1 mM. The carbonate anions steeply decreased with the precipitation of calcite because a great amount of calcium cations (1.0 M) was introduced into the system. Thus, the number of silicate anions became comparable to that of carbonate anions with progress of the crystal growth. We assume that the evolution for the hierarchical self-similar morphology including miniaturization of the growing units was achieved with a gradual increase in the influence of the silicate anions in this system. The presence of silicon was detected on the calcite crystals having a self-similar structure using an EDX microanalyzer equipped on a Hitachi S-4700 field-emission scanning electron microscope. Specific infrared absorption around 900–1100 cm^{-1} observed on the self-similar morphology using a BIO-RAD FTS-165 Fourier-transform infrared spectrometer was assigned to a Si–O stretching mode in alkali–silicate network.[18] These results suggest that polymerized silicate containing calcium cations was formed on the surface of calcite. However, an obvious membrane covering the crystals was not observed on the surface by SEM and TEM images while aragonite crystals produced in silica gel were individually enveloped with a silicate sheath.[19] The adsorption of impurities on crystal surfaces usually suppresses the regular growth and changes the habit or appearance of crystals. It has been reported that morphological evolution of calcium carbonate was induced with the adsorption of several organic molecules.[2–4] In this study, the appearance of a regular rhombohedron with the{10–14} planes was changed into fibrous morphologies elongated along the {11–20} planes. This indicates that silicate anions were specifically adsorbed on the planes parallel to the c axis. Linear alignments of carbonate anions are arranged on the {11–20} planes as shown in Fig. 3. When silicate anions are adsorbed at the anion sites instead of carbonate, they are easily polymerized with dehydration and form a linear chain of polysilicate on the surface. The polymerized chains strongly adsorb on the surface and then prevent the regular growth, in contrast with simple and weak adsorption of other impurities. In the early stage, the basal threefold rotation symmetry attributed to the c axis of the regular rhombohedral shape of calcite (Fig. 2a) was formed because the concentration of silicate anions was lower than that of carbonate. The influence of silicate anions gradually increased with a decrease in the carbonate concentration. First, weak adsorption of silicate anions on the {11–20} planes suppressed the regular growth and induced elongation of the crystals along the c axis (Fig. 2b). The gradual increase in the influence of silicate on the crystal growth induced formation of three-pointed star-like morphology. Irreversible adsorption of the polymerized silicates on the surface promoted fine branching of the growth and reduced the size of the three-pointed stars on the basal crystal (Fig. 2d). Finally, a hierarchical self-similar morphology ranging from nano- to macro-scales was achieved in the progressive stage. However, the calcite crystals were not completely covered with a silicate membrane which was observed on porous aragonite grown in silica gel.[19] The formation of the silicate membrane on the crystal is attributable to the presence of a surface totally consisting of anion sites such as the aragonite {110} planes.

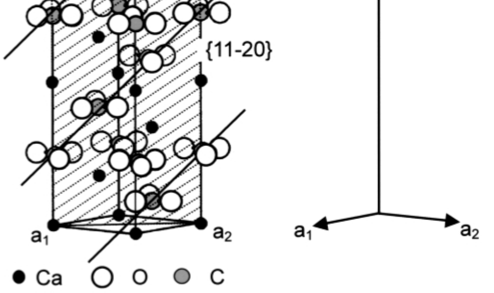

Fig. 3 Schematic drawing of the calcite {11–20} plane and alignment of carbonate anions on the face.

Notes and references

† *Experiments*. We prepared calcite crystals having a hierarchical morphology using a technique based on the method reported by García-Ruiz *et al.*[12–16] However, the formation of single calcite crystals with the hierarchical structure was observed only at lower carbonate concentrations than that adopted by them. Calcium carbonate crystals were prepared by mixing calcium cations with carbonate anions in silica gel using a simple test tube system. Silicate solutions containing carbonate ions (1–100 mM) were produced by addition of 14.9 g sodium metasilicate nonahydrate (98%, Wako) and a certain amount of sodium carbonate (99.5%, Jyunsei) into 200 g purified water. The solutions adjusted to a pH of 7 to 11 with hydrochloric acid gradually changed into sol and then gel. A calcium chloride (99% Wako) solution at a concentration in 1.0 M was poured onto the silica gel. The silica gel loaded with the calcium solution was kept at room temperature. Glass slides as a substrate were previously immersed in the solutions before gelation. The products deposited on glass slides were used for the characterization because silica gel covering the products on the substrate was easily removed by washing with purified water.

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