Development of Ordered Calcium Carbonate Microarrays from Polymorph Specific Planar Films

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Ordered microarrays of rectangular calcite, platy vaterite and spicular aragonite were selectively obtained through overgrowth from planar films prepared with polymeric species. We successfully visualized the polymorphs of the calcium carbonate films using the overgrowth technique.

Biominerals have provided inspiration to try novel strategies in material processing in an ambient atmosphere. One of the applications of biomimetic mineralization that has a high growth potential is the formation of exquisite nano/micro structures consisting of organic–inorganic composite materials in an aqueous solution.[1] Many trials for the structural control of various minerals using organic macromolecules have been reported.[2] It is well known that the presence of organic polymers having carboxy groups,[3–9] such as poly(acrylic acid), influenced the morphology of calcium carbonate, which is the most commonly used biomineral. Especially, 2D films similar to a nacreous layer were obtained with miniaturized crystals of calcium carbonate on glasses,[3,4] cellulose, chitin and its derivatives,[5–8] and poly(vinyl alcohol) film.[9] However, it has been difficult to determine the crystal structure and orientation of the unit crystals in the deposited films because the diffraction signals were weak because of small sizes of crystalline grains for characterization. Moreover, although development of the planar films into controlled 3D forms would be essential for mimicking the biomineralization and the application for the nanoscale fabrication, few reported about 3D structures on a plane,[10] the routes for the morphological evolution has not been identified yet. The enhancement of the crystallographic feature by overgrowth has been reported for determination of the orientation of the biominerals.[11,12] Recently, highly oriented calcite crystals were prepared by epitaxal overgrowth on thin films of calcium carbonate.[13] This letter shows polymorph specific morphological evolution of planar calcium carbonate films. The overgrowth without any additives was an excellent technique for the formation of ordered microarrays and clarification of the polymorph and orientation of the basal films.

Basal planar crystals of calcium carbonate were produced in accordance with previous studies.[7] Chitosan-coated glass slides were immersed in a calcium choloride solution containing PAA. Carbon dioxide gas generated from ammonium carbonate was then introduced into the solution in a closed vessel. After a specific amount of time, the glass substrates were removed form the solution, washed with water, and dried at room temperature. The polymorphism of the obtained planar crystals on the chitosan surface was determined by a standard X-ray diffraction technique (XRD, Rigaku RAD-C) and a microdiffraction system (Rigaku RINT-RAPID). Subsequent overgrowth on the underlying calcium carbonate planar films was performed in a 20-mM calcium chloride solution without any additives by the introduction of carbon dioxide.

By this method, a mixture of calcite, vaterite, and aragonite films was usually obtained on a chitosan surface, although the major crystal structure was influenced by the temperature and molecular weight of PAA.[14] Figure 1 shows SEM images and XRD patterns of the planar films of calcium carbonate in the presence of various concentrations and molecular weights of PAA. Although all the films shown in (a) and (b) of Figure 1 exhibited a planar morphology with a smooth surface, the difference of diffraction patterns indicated that the crystals in areas A, B, and C were calcite, vaterite, and aragonite, respectively. In general, the diffraction peaks were weak and broadened because the planar films consisted of fine grains <50 nm covered with the polymeric molecules having carboxy groups. The specific habits derived from the polymorph disappeared in the films. Thus, the crystallographic orientation was generally unclear in the deposited crystals.

By subsequent overgrowth in a calcium chloride solution without any additives, we observed the development of specific morphologies (Figures 1c–1e) and an increase of the diffraction peaks (Supporting Information). Basically, the crystal structure of the underlying basal films was inherited by the daughter crystals regardless of the existence of PAA. On the other hand, the polymorph specific morphologies were three-dimensionally evolved by the overgrowth. A mosaic array of rhombohedral grains (Figure 1c) was produced on the calcite films (A in Figure 1a). The orientation of the calcite units was partially coordinated; namely, the *c* axis or the $\langle 104\rangle$ direction was perpendicular to the surface of the substrate. Thin plates of vaterite were arrayed along the diameter line perpendicularly to the surface (B in Figure 1a). The *c* axis parallel to the surface radiated from the center of the circular disks (Figure 1d). The *c* axis of the underling vaterite film was also confirmed to be parallel to the surface by the XRD measurement (Supporting Information). A forest of microstyluses appeared on the aragonite films (Figures 1b and 1e). The styluses exhibited a typical form of a pseudohexagonal crystal of aragonite. The *c* axis of aragonite extended upward from the surface. The latent crystallographic habits and orientation of the film were visualized by the subsequent overgrowth. Moreover, 3D microstructures consisting of oriented units spontaneously developed from the 2D morphology. When isolated circular films having a smooth surface were used as a base, we successfully obtained ordered arrays of calcite rhombohedral blocks, vaterite high-aspect walls, and aragonite hexagonal rods as shown in Figure 2.

We previously reported that silicate anions induced the film formation of calcium carbonate on the chitosan substrate.[15] The crystal structure of the silicate-mediated films was not clear because the X-ray diffraction from the films was vague. We found a beautiful concentric array of thin walls developed on the silicate-mediated calcium carbonate film after the subsequent

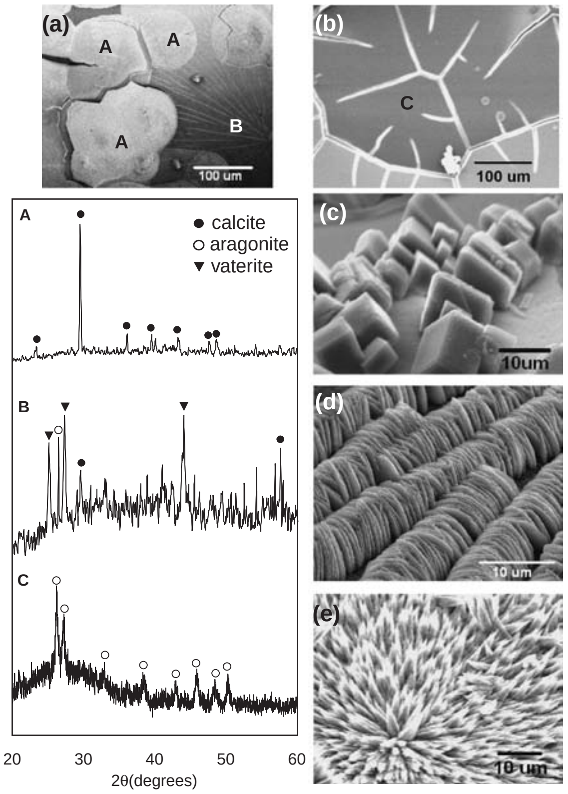

Figure 1. SEM images of calcium carbonate films on a chitosan substrate and their X-ray diffraction patterns. A film containing area A and B was obtained for 9 h with 2.4×10^{-3} wt % of PAA2k. A film containing area C was obtained for 3 days with 2.4×10^{-3} wt % of PAA90k. Areas A, B, and C were determined as calcite, vaterite, and aragonite, respectively. Daughter crystals developed on A, B, and C were shown in (c), (d), and (e), respectively.

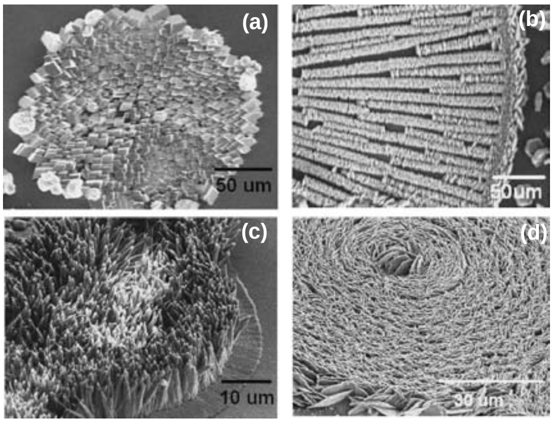

Figure 2. SEM images of ordered microarrays on calcium carbonate circular films after subsequent growth. (a) Calcite rhombohedral blocks on a calcite film obtained for 7 h with 2.4×10^{-3} wt % of PAA2k. (b) Vaterite high-aspect walls on a vaterite film obtained for 9 h with 2.4×10^{-3} wt % of PAA2k. (c) Aragonite styluses on an aragonite film obtained for 1 day with 2.4×10^{-3} wt % of PAA90k. (d) A concentric array of thin vaterite walls on a vaterite film obtained for 3 days with silica gel (pH 10.5).

growth (Figure 2d). Thus, the basal film was determined to be dominantly composed of vaterite. This demonstrates that the subsequent overgrowth technique is available for the development of the polymorphism and the crystallographic orientation of calcium carbonate in 2D films regardless of the inorganic and organic mediators.

The crystal grains of calcium carbonate were miniaturized by coverage of PAA or silicate anions, and the miniaturized grains were two-dimensionally assembled with a guide of anionic molecules anchored to chitosan on a surface.[5–7,15] A supersaturated condition for calcium carbonate without any additives weakened the coverage of the polymerized species and promoted the 3D growth of daughter crystals. In this case, the crystallographic properties of the basal film were inherited by the daughter grains. The ordered structures were produced by periodic generation of embryos of the daughter crystals for the 3D growth, in which the frequency was determined by the balance between the inhibition by the coverage and the promotion with the degree of supersaturation. Finally, the ordered arrays of specific microstructures originated from the habit of the basal crystals. The alternation of the growth mode from 2D into 3D by controlling the influence of the polymeric species would be essential for understanding and mimicking the microfabrication process for the exquisite hierarchiral architectures observed in biominerals.

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References and Notes

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