Formation of Silicate-mediated $CaCO_3$ Films

Akiko Kotachi, Takashi Miura, and Hiroaki Imai*
Department of Applied Chemistry, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku, Yokohama 223-8522

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We successfully obtained silicate-mediated $CaCO_3$ films on a chitosan surface in an aqueous solution system. The presence of silicate anions induced the miniaturization of the carbonate crystals and two-dimensional growth with the arrangement of the miniaturized subunits on the functional surface. The mortar-like effects of silicate anions on the morphological evolution were quite similar to those of organic polyelectrolytes having carboxy groups, such as poly(acrylic acid).

Biominerals are highly organized crystals prepared in aqueous solutions under soft conditions. Biomineralization inspires us to find new processes of material synthesis to realize functional microstructures. Studies of $CaCO_3$ film formation mediated by organic macromolecules containing carboxy groups were reported as interesting approaches for mimicking the mineralization of nacres. These films were produced in supersaturated solutions containing a small amount of poly(acrylic acid) (PAA) or poly(aspartic acid) (PAsp) on a suitable surface, such as a Langmuir–Blodgett film with carboxy groups[1] at the solution–air interface or polysaccharide films on a substrate.[2–6] However, the mechanism of the film formation, including the roles of the coexisting polyelectrolytes and specific surfaces, is not sufficiently understood. Silica is another typical biomineral found in the skeletons of protozoans and mollusks with $CaCO_3$. Thus, knowledge of the interactions among $CaCO_3$, silica and organic macromolecules is essential for the understanding of biomineralization. Garcia–Ruiz et al. reported that many peculiar forms of alkaline-earth metal carbonates were obtained in high-pH silica gel,[7,8] which indicated that silicate anions strongly interact with carbonates, such as $CaCO_3$. We previously clarified that unique architectures, including coral- or petal-like morphologies, can be induced through the miniaturization of the growth subunits by covering the surface of carbonate crystals with silicate anions and by the self-organized assembly of the miniaturized subunits.[9–11] Investigation of the influence of silicate anions on the formation of $CaCO_3$ films on a specific organic surface would be valuable for the clarification of the role of organic surfaces and coexistent electrolytes in biomineralization and would provide new information for tailoring the functional materials in biomimetic methods. This paper describes morphological changes of $CaCO_3$ on a polysaccharide surface with silicate anions and discusses the role of the specific surface and anions compared with the case of PAA.

Precipitation of $CaCO_3$ was performed by the introduction of CO_2 gas generated by the decomposition of $(NH_4)_2CO_3$ into a 20 mM $CaCl_2$ aqueous solution. As a source of silicate anions, silica gel was prepared by the solidification of $Na_2SiO_3{\cdot}9H_2O$ aqueous solution by adjusting the pH to 10.5 with the addition of 0.2 M hydrochloric acid. A solution of $CaCl_2$ previously adjusted to pH 10.5 was poured on the gel. Silicate anions such as $SiO(OH)_3{}^-$ and $Si_4O_6(OH)_6{}^{2-}$ were supplied from silica gel at a basic condition. The saturated concentration of the silicate anions was estimated to be ca. 50 mM at pH 10.5.[12] We added PAA into another calcium chloride solution to compare the effect of silicate anions with that of PAA. The concentration of PAA was fixed to 2.4×10^{-3} or 7.2×10^{-3} wt % according to the results of the previous studies.[3–6] Bare and chitosan-coated glass slides were used as substrates. Chitosan films were prepared on glass slides by spin-coating of an acetic acid solution of chitosan. The chitosan coats were neutralized with an ammonia solution and dried in an electric oven at 100 °C for 30 min. After these substrates were immersed in the calcium solutions, they were placed in a desiccator filled with CO_2 gas from $(NH_4)_2CO_3$ for one day.

Rhombohedral forms of calcite were mainly obtained in the solutions in the absence of coexistent electrolytes, such as silicate anions and PAA (Figure 1). In the presence of silicate anions, we observed aggregates of miniaturized calcite crystals on a bare glass surface (Figure 2a). These facts are consistent with our previously reported results.[9–11] On the other hand, discoid films were observed on a chitosan surface (Figure 2b). A SEM image of a crack at the top face of this discoid film (Figure 2c) showed that the film was composed of small grains. The presence of calcite, aragonite and vaterite was confirmed from X-ray diffraction patterns of the films although the crystal form and orientation of individual small subunits were not determined. The discoidal form suggests that these films were produced by a radial arrangement of the miniaturized subunits on the specific surface. A small navel, which was frequently observed at the center of the films, indicated an initial nucleation site. In our previous studies,[9–11] the miniaturized carbonate crystals were confirmed to be covered with silica. In this case, we deduce that these polycrystalline films are also composed of small $CaCO_3$ subunits covered with silica because the existence of silicon was detected in the products by energy-dispersive X-ray analysis. The ratio of silicon and calcium contained in the films was determined to be ca 3:7 in mol. The presence of a great amount of silicon suggests that each small crystal grain is totally surrounded with silica. Figure 2d shows an image of the grains at a crack of a discoid film after immersion into a 0.1 M NaOH aqueous solution for one minute. We clearly observed the outline of the grains after the treatment because silica covering the carbonate crystals was removed in the alkali solution. It indicates that silica existed between carbonate grains in the films as mortar in a brick wall. After the treatment, the diameter of a crystal grain was easily estimated to be 50–60 nm.

The addition of PAA to the calcium chloride solution induced the formation of aggregates of miniaturized $CaCO_3$ subunits on bare glass (Figure 3a) and discoid films on a chitosan surface (Figure 3b), respectively. These results indicate that silicate anions and organic polyelectrolytes having carboxy groups

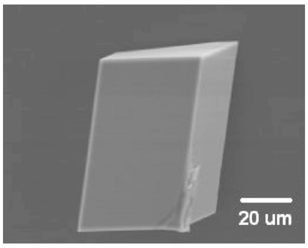

Figure 1. A SEM image for $CaCO_3$ crystals produced in the absence of silicate anions.

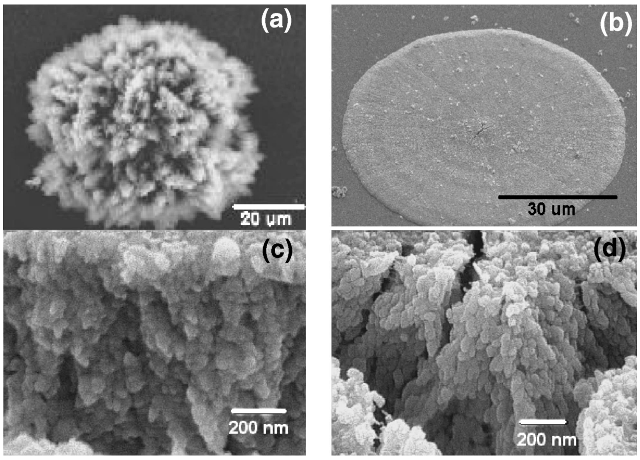

Figure 2. SEM images for $CaCO_3$ crystals produced in the presence of silicate anions on a bare glass plate (a), and in the presence of silicate anions on a chitosan surface (b). Images of a crack before and after a NaOH aqueous solution treatment are shown in (c) and (d), respectively.

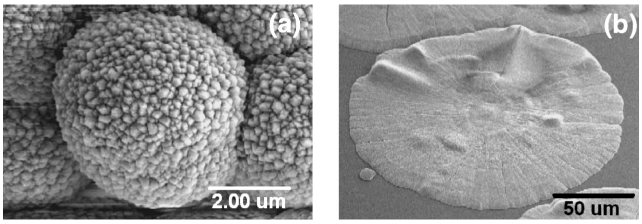

Figure 3. SEM images for $CaCO_3$ crystals produced in the presence of PAA ($M_w = 2000$) (a) on a bare glass plate with 7.2×10^{-2} wt % of PAA, and (b) on a chitosan surface with 2.4×10^{-3} wt % of PAA.

have similar specific influences on the crystal growth of $CaCO_3$. We proposed the polymerization of adsorbed silicate anions on the surface of carbonate crystals. Thus, anionic polymers covering $CaCO_3$ crystals generally inhibit regular growth and miniaturize growth subunits. The subunits miniaturized with PAA were also arranged and then formed a discoid on the chitosan surface.

Whereas spherical or shapeless aggregates were formed on a bare glass surface, definite discoid films were grown on a chitosan surface. The circular forms indicate that the films were produced through a two-dimensional arrangement of the miniaturized subunits from the center. Since the films were not produced on a chitosan surface without the coexistent polyanions, the combination of the insoluble alcoholic substrate and soluble polyanions having negatively charged groups similar to carbonate anions, such as silicate, is essential for morphological evolution. Anionic species cannot be adsorbed on bare glass substrates because the surface is negatively charged in neutral and basic solutions. On the other hand, a chitosan surface having non-ionic alcoholic hydroxy groups effectively adsorbs soluble polyanions through hydrogen bonds. Since polyanions anchored on the surface of the substrate promoted the formation of $CaCO_3$ crystals, the growth of the film occurred only at the edge of the circle. Eventually, discoidal forms were produced through the outgrowth with a two-dimensional arrangement of the miniaturized $CaCO_3$ grains on the surface. The navel at the center is inferred to be formed by the upward growth of the nucleus in the initial stage. The polymorph of $CaCO_3$ was also influenced by specific interaction with the surface because the mixture of calcite, aragonite and vaterite was obtained only on the surface.

In conclusion, $CaCO_3$ films were produced on a chitosan surface by the mediation of silicate anions. Miniaturization of the growth subunits by the adsorption of specific polyanions was essential for morphological evolution. A surface having high adsorbability for anionic species strongly regulated the two-dimensional assembly of the miniaturized subunits through anchored polyanions and thus promoted the formation of discoid films of $CaCO_3$ crystals.

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