

Silicate-Mediated Film Formation of Alkaline-Earth Metal Carbonates

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Discoid films of calcium, strontium and barium carbonates were prepared on the surface of insoluble polyalcohol, such as chitosan, in aqueous solution systems containing silicate anions. Two-dimensional assembly of carbonate crystals covered with silica skin was achieved on the specific surface.

Key words: biomimetic, aquatic chemistry, carbonates, self-organization, templating

1. INTRODUCTION

Silica and calcium carbonate are a typical biomineral. For example, the main compound of the exoskeleton of diatoms is amorphous silica, and eggshells, seashells and corals consist of calcium carbonate. Recently, it is found that biologically produced calcium carbonate crystals perform as a microlens [1]. It demonstrates the potential of the biomineralization process for synthesis of functional materials with sophisticated architectures. Garcia-Ruiz et al. [2-5] reported that the presence of silicate anions obviously changed the morphology of alkaline-earth metal carbonates into peculiar forms, such as fibrils and twisted ribbons. Coral-like porous structures of calcium carbonate were also observed using a similar system containing silicate anions [6]. These results indicate that silica is highly interactive with carbonate crystals and influences the morphological evolution. On the other hand, many reports showed the production of a laminated structure consisting of calcium carbonate films using electrolytes of poly (aspartic acid) (PAsp) and (acrylic acid) (PAA) [7-13]. Calcium carbonate films inspired by nacre were prepared on a porphyrin monolayer and a substrate coated with insoluble polyalcohols and poly (vinyl alcohol) (PVA). The two dimensional architecture of the crystal was obtained by heterogeneous nucleation on the specific surfaces and growth control with the co-existing electrolytes. Here, we report that silicate anions are also utilized for the film formation of alkaline-earth metal carbonates on a polyalcohol substrate. The substructures of the two-dimensional architecture are clearly found using aragonite-type crystals, such as strontium and barium carbonates.

2. EXPERIMENTAL

In this study, we prepared calcium, strontium, and barium carbonates in their chloride aqueous solutions containing silica gel prepared by neutralization of sodium silicate. The pH was adjusted to pH 10.5 [6, 14] to provide silicate anions, such as $\text{SiO}(\text{OH})_3^-$, $\text{Si}_2\text{O}_6(\text{OH})_6^{2-}$, $\text{SiO}_2(\text{OH})_2^{2-}$, from the silica gel into the solutions. The concentration of the silicate anions under the condition was ca. 50 mM [15]. Glass slides were spin-coated with an acetic acid solution of chitosan,

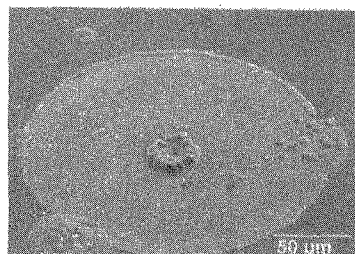
neutralized by ammonium water and dried in an electrical oven at 100 °C for 30 minutes to prepare an insoluble alcohol substrate. Carbonate ions were supplied by introduction of carbon dioxide gas generated with decomposition of ammonium carbonate. The precursor solutions containing 10-20 mM of the alkaline-earth metal chlorides were poured on the silica gel and chitosan-coated glass slides, and then were placed in a desiccator with ammonium carbonate for one to three days under ambient atmosphere.

3. RESULTS AND DISCUSSION

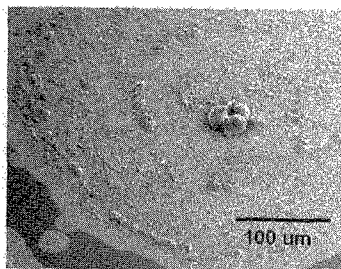
The presence of silicate ions induced the formation of thin films of calcium, strontium and barium carbonates on a chitosan substrate. Typical SEM images (Fig. 1) show that the morphologies of the films were almost the same discoid form. The results of X-ray diffraction indicated that the calcium carbonate films were composed of calcite, aragonite and vaterite. Small grains with a diameter of ca. 20 nm were found on the surface and at the cross section of the films. The outline of the grains was defined after immersion of the films into a 0.1 M sodium hydroxide (NaOH) solution. According to our previous studies [6, 14], the small carbonate grains grown with silicate anions were covered with silica skin. The NaOH treatment removed the skin through dissolution of silicate. Thus, the films consisted of small carbonate grains covered with silica skin. However, details in the substructure including crystallographic orientation were not clarified because the films were a composite of the polymorphs [16].

Because strontium and barium carbonates generally exhibited an aragonite-type structure, the substructure of the products would be easily characterized. As shown in Fig. 2, veins grown from a hexagonal base at the center of a barium carbonate film were observed. The hexagonal habit clearly appeared on the veins after removal of silica skin with immersion into the NaOH solution (Fig. 3). Many steps, terraces and stacking layers were constructed by regular arrangement of small hexagonal subunits. We observed the cast-off skin after dissolution of the carbonate crystals by the immersion into an ethylenediaminetetraacetate (EDTA) solution (Fig. 4). The original morphology of the microstructure

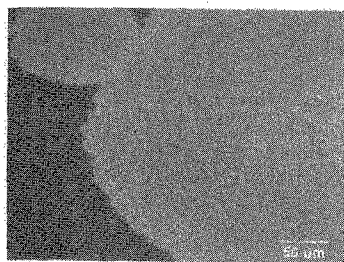
of the films almost remained with silica-rich residue whereas the thickness slightly decreased after the treatment. These results indicate that the carbonate subunits were totally covered with silica skin. An intense signal due to the (002) plane in an X-ray diffraction pattern (Fig. 5) and the hexagonal habits of the subunits indicate that the *c* axis of the aragonite-type crystals in the films were perpendicular to the substrate.



(a) Calcium carbonate



(b) Strontium carbonate



(c) Barium carbonate

Fig. 1 SEM images for discoid films of various kinds of alkaline-earth metal carbonates grown on a chitosan substrate in the presence of silicate anions.

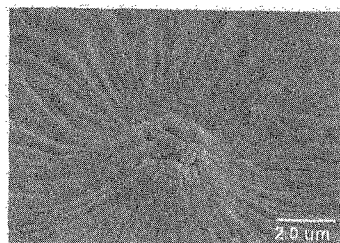


Fig. 2 A SEM image for veins grown from a basal hexagon at the center of a barium carbonate film.

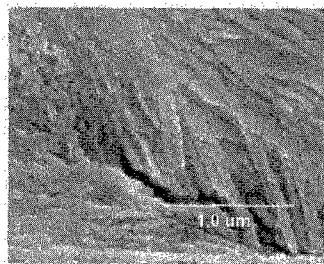


Fig. 3 A SEM image for veins of a barium carbonate film after NaOH treatment.

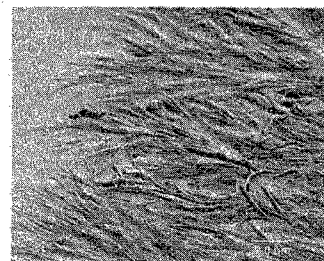


Fig. 4 A SEM image for silica residue of a barium carbonate film after EDTA treatment.

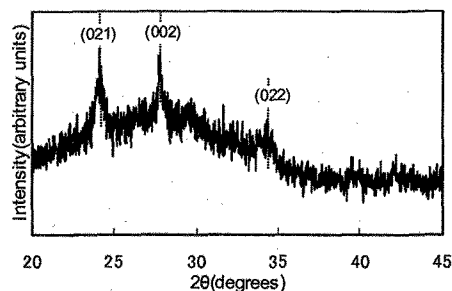


Fig. 5 An X-ray diffraction pattern of the barium carbonate film. The indices for the aragonite-type crystal were indicated.

The veins consisting of small hexagonal subunits were radiated from the center and densely branched as a two-dimensional dendrite (Fig. 6). The hexagonal subunits covered with silica skin were assembled from the basal crystal at the center with a certain regularity on the substrate. The adsorption of silicate anions induced the miniaturization of barium carbonate crystals and the formation of the planer films through radial growth of the hexagonal subunits. The crystallographic orientation of the subunits of was regulated in the barium carbonate films although the subcrystals were randomly arranged in the calcium carbonate ones. It means that the restriction of the crystal growth with silica was relatively weak for the aragonite-type crystals.

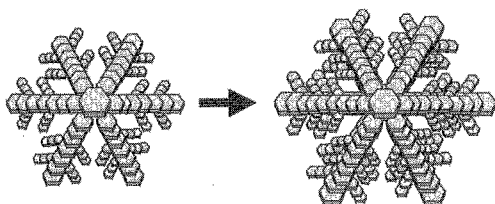


Fig. 6 A schematic model for two dimensional dendritic growth of aragonite-type carbonate on an insoluble alcohol substrate. The c axis of the subunits is perpendicular to the substrate.

The two-dimensional growth was induced by silicate anions anchored on the chitosan surface. The arrangement of the c axis of the aragonite-type films was also ascribed to the conformation of the multimeric silicate anions (Fig. 7). Because the distance of the ionic sites of the silicate chain (0.525 nm) was close to that of the carbonate sites on the (001) plane of barium carbonate (0.531 nm) and strontium one (0.511 nm), the anchored silicates performed as a template of oriented nucleation and guided growth on the surface.

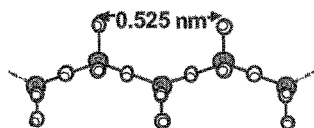


Fig. 7 A schematic model for the distance between ionic sites of multimeric silicate anions.

The two-dimensional dendrite of strontium carbonate was grown at pH 9.5 (Fig. 8). Because the concentration of silicate anions was lower than that at pH 10.5, the restriction of the crystal growth with the adsorption was relatively small at that condition. Thus, the definite shape was clearly observed.

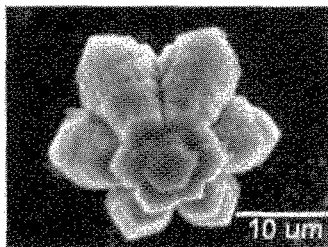


Fig. 8 A SEM image for a two-dimensional dendrite of strontium carbonate grown at pH 9.5 in the presence of silica gel.

4. CONCLUSIONS

The presence of silicate anions induced the film formation of alkaline-earth metal carbonates on an insoluble polyalcohol substrate, such as chitosan. The miniaturization of the carbonate crystals and template effects for the nucleation and guided growth with silicate anions were essential for the morphological evolution. Discoid films were produced through two-dimensional growth of miniaturized carbonate crystals guided by silicate anions anchored on a chitosan surface.

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