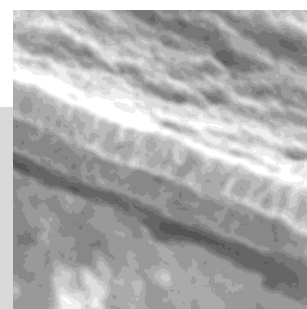


# Polymer/Calcium Carbonate Layered Thin-Film Composites

By Takashi Kato\*

*Formation of the nacre of a shell is mimicked here to synthesize layered polymer/calcium carbonate composites such as that shown in the Figure. The combination of insoluble chitin or chitosan solid matrices with soluble acidic macromolecules such as poly(acrylic acid) is used to induce thin-film crystallization of  $\text{CaCO}_3$  on the solid matrices. The polymorph formed can also be controlled employing this method.*



## 1. Introduction

Materials scientists are able to obtain ideas from the structures of living organisms.<sup>[1–7]</sup> Biominerals, a variety of inorganic crystals and their composites with biomacromolecules are nice examples for the design of new hybrid materials because they show controlled morphology and unique properties.<sup>[1–10]</sup> The nacre of shells is an attractive target for the design of organic/inorganic hybrid materials by mimicking biomineralization processes. It forms a layered structure of brick and mortar, which results in the formation of composites with high mechanical strength and unusual optical properties, such as pearl luster.<sup>[1–5]</sup> Figure 1 shows a scanning electron microscopy (SEM) image of the nacre layer and a schematic illustration of its structure. The brick is flat crystals of calcium carbonate ( $\text{CaCO}_3$ ) the thickness of which is less than  $1.0\ \mu\text{m}$ . The mortar consists of organic biomacromolecules, that is, silk-fibroin-like proteins and chitin. These biomacromolecules play a key role in the formation of such layered structures through interactions between their functional groups and calcium ion in vivo.

Calcium carbonate has three types of polymorphs: calcite, aragonite, and vaterite. Calcite is thermodynamically the most stable form, while vaterite is the most unstable form. Aragonite crystals may enhance the mechanical properties of the nacre of the shell because of the absence of cleavage planes.

Synthetic approaches to the fabrication of layered organic/inorganic composites with controlled structures based on calcium carbonate may lead to the fabrication of new materials

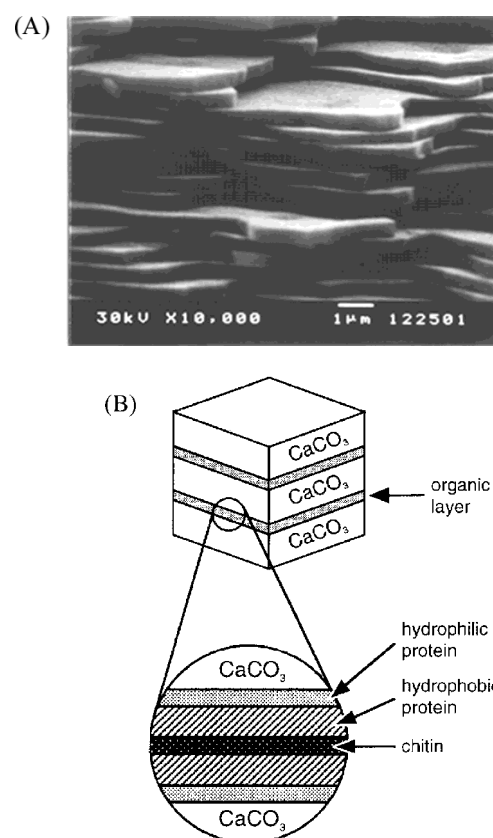


Fig. 1. Layered structure of the nacre of shells. A) SEM image of the cross section of the fractured nacre of abalone. B) Schematic illustration of the layered organic/inorganic structure.

with high performance and high function as well as environmental benignity. Intensive studies have focused on control over the crystal habit, morphology, shape, and size of calcium carbonate in the presence of organic substances.<sup>[1–7]</sup> As for the control of mineralization processes using living organisms, flat aragonite films have been biofabricated between the mantle

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and shell.<sup>[10]</sup> However, *in vitro*, it is not easy to control the mineralization processes. Recently, calcium carbonate thin films were prepared by synthetic approaches.<sup>[11–17]</sup> However, to our knowledge, no layered thin films with homogeneous thickness and controlled polymorphs had been fabricated using simple synthetic procedures until Kato and co-workers successfully prepared thin-film layered composites of calcium carbonate.<sup>[16,17]</sup> To obtain layered composites, more control over the thickness and flatness of the surfaces has to be attained for calcium carbonate crystals. In this article, we describe: 1) thin-film formation of calcium carbonate; 2) fabrication of polymer/calcium carbonate layered composite films; 3) polymorph control over calcium carbonate thin films.

## 2. Thin-Film Crystallization of Calcium Carbonates

It is known that, for controlled crystallization of a mollusc shell *in vivo*, soluble proteins rich in aspartic acid are adsorbed on hydrophobic proteins forming a core layer by complexation with chitin.<sup>[1]</sup> The adsorbed proteins bind calcium ions and induce nucleation of calcium carbonate. In the approach by Kato and co-workers,<sup>[11,12,16,17]</sup> the combination of soluble acidic and insoluble macromolecules with simpler structures was used for the induction of thin-film crystallization. Chitin and chitosan were chosen as solid insoluble matrices for crystallization. Chitin widely exists in organisms in nature. It is a major component of the organic core layer of the nacre. Chitosan is obtained by the deacetylation of chitin. These polysaccharides have functional groups such as OH and NH. The acidic macromolecules poly(acrylic acid), poly(aspartate), and poly(glutamate) were employed as soluble polymer additives. Crystallization of  $\text{CaCO}_3$  on the solid matrices was carried out from a supersaturated aqueous solution of calcium carbonate in the presence of the soluble acidic macromolecules. The polysaccharides, serving as solid matrices for the crystallization, were spin-coated on glass substrates. Figure 2 shows the SEM image of developing thin-film crystals of calcium carbonate on the surface of chitin. Thin films of calcium carbonate are formed on the surface of

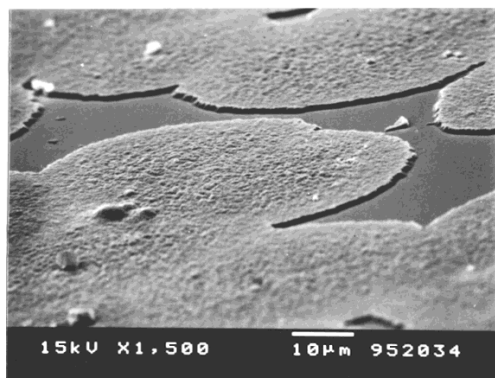


Fig. 2. SEM image of developing thin-film crystals of  $\text{CaCO}_3$  on the surface of chitin in the presence of poly(acrylic acid). Reprinted from [16] with permission from The Chemical Society of Japan (copyright 2000).

the solid matrix only when the acidic macromolecule exists in solution in a specific concentration range. For example, poly(acrylic acid) induces thin-film formation of  $\text{CaCO}_3$  in the range between  $2.4 \times 10^{-3}$  and  $7.2 \times 10^{-3}$  wt.-% ( $3.3 \times 10^{-4}$  and  $1.0 \times 10^{-3}$  mol of carboxylic acid/L). The mechanical stability of the composite film is so high that no flaking is seen on microwave irradiation. A free-standing thin-film composite detached from glass substrates is shown in Figure 3. The film is flexible and its surface is smooth. Thin-film coating of calcium carbonate has also been achieved on chitin fibers in the presence of the acidic macromolecule.<sup>[12]</sup>

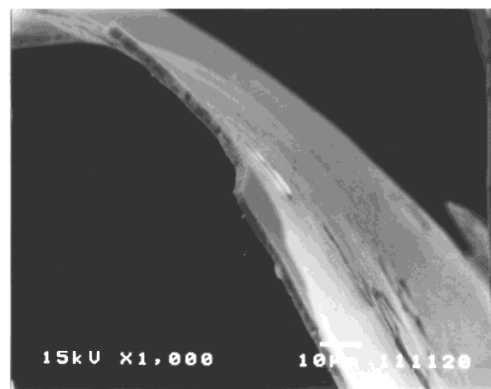


Fig. 3. SEM image of a free-standing film of a chitin/calcium carbonate composite.

In the absence of acidic macromolecules in solution, only rhombohedral calcite crystals  $10 \mu\text{m}$  in size are obtained on chitin and chitosan matrices. On glass substrates that are not coated with organic matrices no thin-film formation is observed even in the presence of acidic soluble macromolecules. In the absence of the solid organic matrices on the glass substrates, poly(amino acid)s such as poly(aspartate) and poly(glutamate) give spherical vaterite crystals, while poly(acrylic acid) inhibits crystallization. These results suggest that neither insoluble chitin nor a soluble acidic macromolecule can alone induce such thin-film development and that the cooperation of the polysaccharides and the acid-rich macromolecules is essential. The OH and NH moieties of chitin and chitosan can interact with carboxylates of the macromolecules in solution, which leads to the adsorption of the acidic macromolecules on the surface. These macromolecules can bind calcium ion on the surface of the chitin films, which results in a local high concentration of the calcium ion on the surface, inducing the nucleation of calcium carbonate. These processes are similar to those considered to occur in biomineralization processes *in vivo*.<sup>[1]</sup> However, they are not yet fully understood.

## 3. Polymer/Calcium Carbonate Layered Composite Films

It is of interest that the synthetic method described above leads to the development of self-organized calcium carbonate thin films with homogeneous thickness of  $0.8 \mu\text{m}$ , which is the

same level as that of calcium carbonate thin-film crystals of the nacre.<sup>[11,12,16]</sup> We expected that layered composite films having structures similar to that of the nacre of shells could be obtained if these coating processes of organic and inorganic films were repeated. The alternate operations of spin-coating the polysaccharide and thin-film crystallization of  $\text{CaCO}_3$  from aqueous solution resulted in the formation of layered composites. An SEM image of the cross section of a double-layered organic/inorganic composite is shown in Figure 4. It reveals that structures composed of bricks of  $\text{CaCO}_3$  crystals and mortar of polymer are obtained. Triple-layered compo-

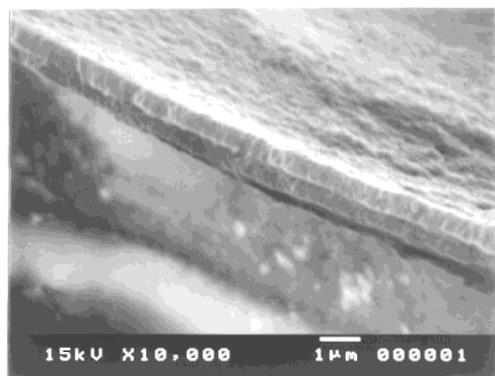


Fig. 4. SEM image of the cross section of a double-layered composite film consisting of  $\text{CaCO}_3$  and chitin prepared in the presence of poly(acrylic acid). Reprinted from [16] with permission from The Chemical Society of Japan (copyright 2000).

sites can also be prepared by the same method. It should be noted that layered structures can be arranged by these simple procedures using simple polymers. More precise control of the homogeneity of the film thickness and the flatness of the surface will lead to the preparation of multilayered composite films.

In biomineralization processes by living organisms, pre-organized layered sheets are considered to serve as a matrix for the crystallization of  $\text{CaCO}_3$ , leading to the brick and mortar structure.<sup>[1–5]</sup> A recent study suggests that in the sheet matrix, ions are able to pass through the pores of the sheets and aragonite crystals grow through the pores, forming mineral bridges between layers.<sup>[9]</sup> It is difficult to mimic the formation of pre-organized polymer assemblies. However, in the synthetic approach reported in this article, simple alternate coating and crystallization processes have enabled us to prepare layered structures.

#### 4. Polymorph Control for Calcium Carbonate Thin Films

Polymorph control of aragonite crystals has been carried out by using the protein extracted from sea shells,<sup>[18]</sup> synthetic polymers,<sup>[19]</sup> and Langmuir–Blodgett (LB) films.<sup>[20]</sup> However, no aragonite thin films had been obtained by the use of simple polymers in vitro. For the thin-film crystallization described in this article, calcite is formed as the major type of polymorph,

while no aragonite is obtained. In these cases only organic molecules are used to control the crystallization.

To prepare aragonite thin films, organic macromolecules were used in combination with magnesium ion ( $\text{Mg}^{2+}$ ),<sup>[17]</sup> because  $\text{Mg}^{2+}$  is known to induce aragonite crystallization.<sup>[21]</sup> It was expected that cooperation of  $\text{Mg}^{2+}$ , chitosan, and acidic macromolecules would lead to the formation of aragonite thin films. Magnesium chloride was added to supersaturated calcium carbonate solution containing poly(aspartate). The ratio of the concentration of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  was 6.0, which is similar to that observed for sea water. An appropriate concentration of an acidic macromolecule led to the formation of  $\text{CaCO}_3$  thin films on chitosan matrices. X-ray diffraction (XRD) patterns (Fig. 5) show that the fraction of aragonite in the films is 95 wt.-% or higher and vaterite is not formed. In contrast, needle morphology is seen on chitosan in the absence of

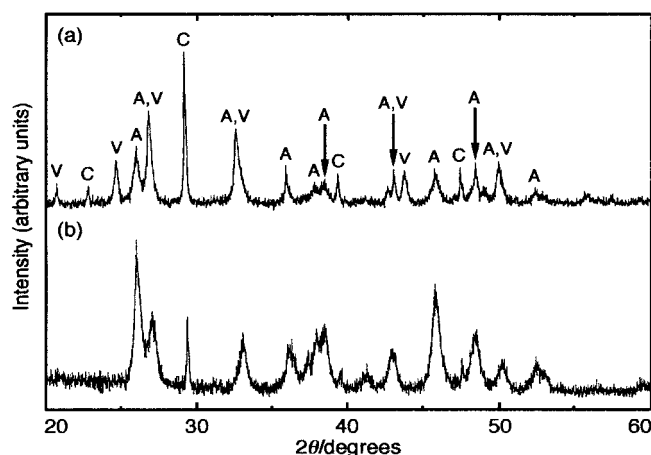


Fig. 5. XRD patterns of  $\text{CaCO}_3$  thin films grown on chitosan matrices in the presence of poly(aspartate): a) in the absence of  $\text{MgCl}_2$ , b) in the presence of  $\text{MgCl}_2$  ( $\text{Mg}^{2+}/\text{Ca}^{2+} = 6$ ). Aragonite (A), calcite (C), and vaterite (V). Reprinted from [17] with permission from The Royal Society of Chemistry (copyright 2000).

acidic macromolecules. The surface of the films is smoother than that obtained without  $\text{MgCl}_2$ . Double-layered aragonite composite films have also been prepared by the alternate operation of spin-coating and crystallization.

#### 5. Conclusion

Organic/inorganic composite materials with organized and/or hierarchical structures on the nanometer or micrometer scale may lead to materials with unique functions and significantly improved mechanical properties. The results reported here offer approaches to a new type of hybrid material. The components of inorganic substances such as calcium carbonate and organic polymers derived from biomolecules give the resultant materials environmental benignity.

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