

博士論文

**Morphology Control and Functionalization of
Polymer/CaCO₃ Thin Film Hybrids**
(高分子／炭酸カルシウム薄膜ハイブリッドの
形態制御と機能化)

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論文題目 Morphology Control and Functionalization of Polymer/CaCO₃ Thin
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Biomaterial is the hard tissues produced by living organisms. The formation process thereof is called biomineralization. Biomaterials are known for their elaborate hierarchical structures and excellent properties. In synthetic systems, formation of hard materials generally relies on high-temperature processes, due to that energy is needed to interrupt the strong interactions between the constituent units of these materials. In contrast, biomaterials are synthesized under environmental conditions. It is therefore promising to develop novel environmentally-benign synthetic approaches through learning from the self-organization process of biomineralization. Previous studies revealed that living organisms employ both soluble and insoluble organic molecules to control crystallization of biomaterials. Inspired by this mechanism, we have been employing the cooperation of soluble acidic polymers and insoluble polymer matrices to control crystallization of CaCO₃. Through this approach, a variety of thin-film CaCO₃ materials were prepared. Here, we further explored this biomimetic approach for crystallization. In this study, two new types of additives, Mg²⁺ ion and supramolecular polyrotaxane, were applied to induce formation of thin-film morphologies of CaCO₃. Attempts to functionalize the thin-film materials of CaCO₃ were also made by employing poly(cyclodextrin) as matrix.

1. Tuning the Stability of CaCO₃ Crystals with Magnesium Ion for the Formation of Aragonite Thin Films on Organic Polymer Templates

Mg²⁺ is essential for the morphology development and functionalization of biominerals. In this chapter, the biomimetic synthesis of CaCO₃ thin films using Mg²⁺ is reported. Thin-film growth of CaCO₃ on annealed poly(vinyl alcohol) matrices is induced by adding Mg²⁺ into the supersaturated solution of CaCO₃. Both the growth rate and surface morphology of the aragonite thin films depended upon the concentration of Mg²⁺ in the mineralization solution. In the absence of poly(vinyl alcohol) matrices, no thin films are formed despite the presence of Mg²⁺. Molecular dynamics simulation of the CaCO₃ precursor suggests that the transition of amorphous calcium carbonate to crystals is suppressed in the presence of Mg²⁺. The role for ionic additives in crystallization of CaCO₃ on organic templates revealed in this study may provide useful information for the development of functional hybrid materials. The details of this study are discussed in original paper [1].

2. Morphology Control of CaCO₃/PVA Hybrids Using the Cyclodextrin-Based Polyrotaxane: Effects of the Carboxyl Groups Locally-Concentrated by Supramolecular Structure

Polyrotaxane has been widely applied in functional materials. However, their use in inorganic synthesis is almost not explored. This chapter reports on the use of polyrotaxane in synthesis of CaCO₃ thin films. α -Cyclodextrin polyrotaxanes functionalized with carboxyl groups were synthesized and characterized. They are

subsequently used as additives in crystallization of CaCO_3 . The presence of carboxylated polyrotaxane as additive induced CaCO_3 crystals in thin-film morphology on poly(vinyl alcohol) matrices. This thin-film growth was not achieved when using the individual carboxylated α -cyclodextrin units. The results suggest that the monomer cyclodextrin units entrapped by polyrotaxane exert a collective effect on CaCO_3 crystallization in spite of their highly mobile characteristics. Previously, covalent polymers were used to induce thin-film growth of CaCO_3 . The use of supramolecular polymer here extended our understanding of the effects of additives in CaCO_3 crystallization. In addition, the results show that morphology of the CaCO_3 thin films can be tuned by using polyrotaxanes with different molecular weights. Thus, the use of polyrotaxane as additive also offered a new approach for crystallization control of CaCO_3 thin films. The details of this study are discussed in original paper [2].

3. Facile Complexation of Dyes with Thin-Film CaCO_3 by Using Poly(cyclodextrin) Matrices

Previously, functionalization of CaCO_3 crystals with hydrophobic molecules requires the use of surfactants or requires chemical modifications of the hydrophobic molecules. This chapter reports on a facile method to complex CaCO_3 materials with hydrophobic dyes by using poly(cyclodextrin) as the matrix to grow CaCO_3 thin films. Poly(cyclodextrin) matrices were prepared by crosslinking cyclodextrins with ethylene glycol diglycidyl ether. Thin-film composites of CaCO_3 and poly(cyclodextrin) were obtained by biomimetic crystallization of CaCO_3 on the

poly(cyclodextrin) matrices. These thin films can conveniently be functionalized with hydrophobic dyes by simply dipping them into the dye solutions. Dye molecules were incorporated into the thin-film composites of CaCO_3 and poly(cyclodextrin) through the host-guest interaction with cyclodextrins. Complexation of CaCO_3 thin films with azo dyes and fluorescent dyes was achieved through this method. The photoisomerization of azo dyes is observed in the thin-film composites. Results obtained in this chapter contributed to the functionalization of thin-film materials of CaCO_3 . The details of this study are discussed in original paper [3].

4. Conclusion and Perspectives

In this thesis, biomimetic synthesis of CaCO_3 thin films was achieved by employing the cooperative effects of soluble additives and insoluble matrices. New types of additives effective for inducing thin-film morphology of CaCO_3 crystals were reported. Moreover, a new approach to functionalize the CaCO_3 thin films was also developed.

In chapter 2 and 3, thin-film morphologies of CaCO_3 crystals were successfully induced by using new types of additives: magnesium ion and polyrotaxane. Control on the development of CaCO_3 thin films has been achieved in the presence of these additives. Use of these new additives not only enriches the approaches of crystallization control, but also facilitates the mechanism study of CaCO_3 crystallization by comparing them with the previously used covalent polymers. Additionally, the use of polyrotaxane as additive for induction of CaCO_3 thin films also provides a possibility to realize stimuli-controlled crystallization. In chapter 4,

hydrophobic dyes are introduced into the CaCO₃ thin films by using poly(cyclodextrin) as matrix. This approach could be useful as well for the functionalization of thin-film CaCO₃ materials with hydrophobic bioactive molecules, which could be important for biomedical applications of these thin films.

In our previous studies, we successfully prepared CaCO₃ thin films and controlled their morphologies by using the cooperation of additive and matrix. However, the formation mechanism of these thin-film states of CaCO₃ is still not clear. The attempts to functionalize these thin films are also limited. The results obtained in this thesis contributed to both the comprehension of the mechanisms involved in the thin-film growth, and to the development of new approaches to prepare and functionalize these thin-film materials.

List of Publications

Original Papers

[1] “Tuning the stability of CaCO₃ crystals with magnesium ions for formation of aragonite thin films on organic polymer templates”

F. Zhu, T. Nishimura, T. Sakamoto, H. Tomono, H. Nada, Y. Okumura, H. Kikuchi, and T. Kato, *Chem. Asian J.* 2013, **8**, p3232.

[2] “Supramolecular effects on formation of CaCO₃ thin films on a polymer matrix”

F. Zhu, T. Nishimura, H. Eimura, and T. Kato, *CrystEngComm* 2014, **16**, p1496.

[3] “Facile complexation of dyes within thin-film CaCO₃ by using poly(cyclodextrin) matrices”

F. Zhu, T. Nishimura and T. Kato, in preparation

References

[1] “Effects of magnesium ions and water molecules on the structure of amorphous calcium carbonate: a molecular dynamics study”

H. Tomono, H. Nada, F. Zhu, T. Sakamoto, T. Nishimura, and T. Kato, *J. Phys. Chem. B*, 2013, **117**, p14849.