博士論文

Development and Structural Control of Organic Polymer/Inorganic Hybrids through Precursor Methods

（前駆体法による有機高分子／無機物複合体の構築と構造制御）

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Biomineralization is a biological process creating organic/inorganic hybrid tissues such as bones, teeth, and shells. Biomineralization is an inorganic crystallization process inside polymer frameworks precisely-controlled by bioorganic molecules. It is noteworthy that this process produces sophisticated ordered structures from abundant natural resources under ambient conditions. Therefore, biomineralization attracts much attention as a promising model for the development of functional materials with controlled ordered structures. One of the key factors in the biomineralization processes is the amorphous inorganic precursors. These precursors are formed by the assistance of biopolymers and they are able to infiltrate into the polymer frameworks with complex structures. After the introduction into the frameworks, they transform to a crystalline state resulting in the nanohybrid structures of biominerals.

Recently, the formation of synthetic amorphous calcium carbonate colloids stabilized by polymer additives has been reported. These amorphous colloids can work as a precursor for crystallization on the organic templates similar to the biomineralization processes in nature. The objective of this thesis is to explore the possibility of the crystallization method using synthetic amorphous precursors aiming at the development of functional materials. In order to design the functions of hybrid materials, the tuning of ordered structures is essential. However, the preparation of complex hybrid structures still remains challenging. One of the promising approaches is to use the self-organized structures of a liquid crystal. It is expected that amorphous precursors penetrate into the liquid-crystalline structures leading to the formation of hybrid ordered structures. In addition to commonly-used calcium salts, the author also focuses on zinc hydroxide compounds. If the structural control of zinc hydroxide is achieved, it will open a new way of preparing functional zinc compound materials with controlled ordered structures.

In the present thesis, the development and structural control of organic polymer/inorganic hybrids through precursor methods are described. In chapter 1, the chitin/calcium carbonate hybrids keeping helical structures have been developed by using liquid-crystalline chitin templates for calcium carbonate crystallization. In chapter 2, the formation of polymer/zinc hydroxide carbonate hybrids and their conversion to zinc oxide thin films have been studied.

Chapter 1. Helically Structured Chitin/Calcium Carbonate Hybrids Mimicking Crustacean Cuticles

This chapter describes the biomineralization-inspired approach to the development of helical chitin/calcium carbonate hybrids mimicking crustacean cuticles. The cuticles of crustacean such as shrimps and crabs consist of mainly chitin and calcium carbonate forming helical structures. In the formation process of crustacean cuticles, amorphous calcium carbonate is introduced inside the helical chitin frameworks and it transforms to the crystalline state. The resultant hybrid tissues exhibit excellent mechanical properties owing to its helical hybrid structures.

The objective of this chapter is to mimic the helical chitin/calcium carbonate hybrid structures of the crustacean cuticles. In order to form the helically ordered structures, the helical self-assembled structure of a cholesteric liquid crystal is used as a template for calcium carbonate crystallization. The strategy in this chapter is to introduce amorphous calcium carbonate precursors inside the helical chitin templates and they are expected to transform to crystals as the biomineralization process in nature. For the preparation of helical chitin templates, chitin whiskers are employed as a constituent. Chitin whiskers are rod-like crystallites of chitin and they are prepared through acid hydrolysis of chitin powders. The dispersion of chitin whiskers results in the formation of cholesteric liquid crystals and the liquid-crystalline structures are fixed by the cross-linked polymer networks to use as a solid template for calcium carbonate crystallization.

The as-prepared template was immersed in the suspensions of amorphous calcium carbonate colloids for calcium carbonate crystallization. After the crystallization process, the samples were examined by the thermogravimetric analyses, which revealed the incorporation of calcium carbonate inside the template. In order to study the hybrid formation mechanisms, the samples were examined by infrared absorption spectroscopy before the calcium carbonate crystallization and after the crystallization processes. Considering the results of infrared absorption spectroscopic studies, it is assumed that the carboxyl groups of the cross-linked polymer networks coordinate to calcium ions, which induces the incorporation of amorphous calcium carbonate precursors inside the chitin template. These precursors transform to the crystalline state after aging which is more thermodynamically favored. These results indicate that the carboxyl groups may play a key role in the calcium carbonate hybrid formation in this precursor-mediated crystallization processes.

In order to study the details of the hybrid structures, the hybrid was observed by the scanning electron microscope. The helical alignment of chitin whiskers was observed in the cross sections of the samples. The half pitch of the helical order increases after the crystallization processes, which suggests the incorporation of calcium carbonate inside the helical structures. The energy-dispersive X-ray analyses on the hybrid reveals that calcium carbonate is uniformly distributed inside the chitin template. The observation by transmission electron microscope elucidates that calcium carbonate nanocrystals are dispersed inside the chitin template. Therefore it is estimated that the use of amorphous calcium carbonate precursors results in the formation of calcium carbonate nanocrystals uniformly distributed inside the helical chitin template.

In conclusion, the development of uniform chitin/calcium carbonate hybrids keeping helical structures is achieved for the first time. It is expected that this helically ordered structure endows hybrid materials with substantial mechanical properties. The details of this study are discussed in paper [1].

Chapter 2. Formation of Polymer/Zinc Hydroxide Carbonate Hybrids toward the Development of Zinc Oxide Thin Films

This chapter describes the formation of polymer/zinc hydroxide carbonate hybrids and their conversion to zinc oxide thin films. Zinc hydroxide carbonate is a useful precursor for the syntheses of zinc oxide materials. If the structural control of zinc hydroxide carbonate is achieved, it can be converted to zinc oxide keeping its structures. Zinc oxide is a versatile metal oxide which can be used as electrodes, photocatalysts, phosphors, semiconductors and so on.

Herein, the formation of polymer/zinc hydroxide carbonate hybrids using amorphous precursors and their conversion to zinc oxide have been studied. The amorphous zinc hydroxide carbonate was formed by using a polymer additive. The results of thermogravimetric analyses and the X-ray diffraction measurements suggest that the polymer additive inhibits the crystallization of zinc hydroxide carbonate and stabilizes the amorphous phase. The solution containing this amorphous compound was used as a precursor for zinc hydroxide carbonate crystallization on the polymer matrix. The spin-coated polymer matrix was immersed in the crystallization solution, leading to the spontaneous formation of thin film crystals. When we used the solution without the addition of polymer additives, these thin film crystals were not obtained. Therefore, the amorphous precursors are needed for this crystallization process. The observation of these thin films by scanning electron microscope and transmission electron microscope revealed that the nanocrystals are formed inside the polymer matrices and they grow radially to form the spherulitic thin films. The results of X-ray diffraction measurements on the resultant hybrid sample suggest that the zinc hydroxide carbonate crystals inside the hybrid align along the (002) plane parallel to the substrate and (200) plane perpendicular to the substrate.

The resultant zinc hydroxide carbonate crystals were converted to zinc oxide by thermal treatment. After the conversion, the morphology of the sample was studied by scanning electron microscope observation. The converted sample keeps its thin-film morphology and it consists of granular nanocrystals forming porous structures. The results of thermogravimetric analyses suggest that the polymer matrices were completely decomposed during the conversion process. The results of X-ray diffraction measurements suggest that the zinc oxide crystals align along the (002) plane parallel to the substrate. Because the zinc hydroxide thin films before the conversion also had the parallel orientation of (002) plane, it is assumed that the crystallographic orientation is retained after the conversion. The photocatalytic function of resultant zinc oxide thin films was studied by the photocatalytic degradation experiment of 2-propanol. The consumption of 2-propanol and the generation of acetone were detected by gas chromatography, which clearly indicates the photocatalytic oxidation of 2-propanol caused by zinc oxide thin films.

In conclusion, the biomineralization-inspired precursor-mediated approach to the development of zinc oxide thin films was demonstrated for the first time. The details of this study are discussed in paper [2].

Chapter 3. Conclusion and Perspective

The present thesis describes the extended possibility of the biomineralization-inspired precursor method.

In chapter 1, the helical chitin/calcium carbonate hybrids mimicking crustacean cuticles are reported. The development of three-dimensionally ordered structures of hybrid materials are achieved by using amorphous calcium carbonate precursors. In chapter 2, the zinc oxide thin films are prepared through the conversion of hybrid thin films which are formed by using amorphous zinc hydroxide carbonate precursors. The development and structural control of functional inorganic materials has been demonstrated by the precursor-mediated crystallization method.

The results shown in this thesis offer a valuable concept that the precursor method is useful for the development of complex hybrid structures and can be applied not only to calcium carbonate but also to the zinc-based compound materials. The biomineralization-inspired methods have many advantages such as low cost, low energy consumption, and the ease of large scale production. Therefore, the approach in this study contributes to the field of materials science. And it is expected that this biomineralization-inspired approach using amorphous precursors will lead to the development of novel functional materials in the future.

List of Publications

Original Papers

[1] "Formation of Helically Structured Chitin/$CaCO_3$ Hybrids through an Approach Inspired by the Biomineralization Processes of Crustacean Cuticles"
Shunichi Matsumura, Satoshi Kajiyama, Tatsuya Nishimura, Takashi Kato
Small **2015**, *11*, 5127.

[2] "Biomineralization-Inspired Preparation of Zinc Hydroxide Carbonate/Polymer Hybrids and Their Conversion to Zinc Oxide Thin-Film Photocatalysts"
Shunichi Matsumura, Yoshimasa Horiguchi, Tatsuya Nishimura, Hideki Sakai, Takashi Kato
Chem. Eur. J. in press.