SUMMARY OF Ph.D. DISSERTATION

School	Student Identification Number	SURNAME, First name
Integrated Design Engineering		OAKI, Yuya

Title

Hierarchical Crystal Design with an Exquisite Association of Polymer Matrix and Molecular Recognition: Approaches Learned from Biominerals

Abstract

Biominerals have attracted much interest because of their seemingly well-designed morphologies and hierarchical structures, which provide versatile properties. The architecture emerging from self-organization under ambient conditions provides a sophisticated model for materials science. The macroscopic structure, morphology, incorporated macromolecules, and emergent properties in various carbonate-based biominerals have been well reported. On the other hands, the structures under submicrometric scales are not fully understood at this time. The biomimetic approach for crystal design using organic polymers has also been demonstrated in various combinations of crystals and polymers. Typical polymer-mediated crystallization, as previously reported, only resulted in the morphological modification within zero- to two-dimensional nanostructures. It is not easy to approach a real biomineral because it is so complex and elaborate. Simultaneous pursuit of a sophisticated composite and hierarchical structure is especially difficult using current technology. In this paper, I investigated the nanoscopic architectures in real biominerals and developed the biomimetic approach for hierarchical crystal design from nanoscopic to macroscopic scales.

Chapter 1 summarizes the background and earlier works related to this study, and then mentions the objective of this thesis.

Chapter 2 describes the nanoscopic structures in real biominerals. The composite architecture of nanocrystals 20–100 nm in size and biopolymers resided in nacreous layer, stereom of sea urchin spine, coral, and foraminifer. The nanocrystal engineering led to the macroscopic morphogenesis.

Chapter 3 shows the macroscopic morphological control of crystals using polymer matrix. The morphology of crystals grown in polymer matrix was changed from polyhedral shapes to dendritic forms via skeletal morphology with increasing the polymer density, regardless of the sorts of crystals and polymers. Diffusion-controlled growth was achieved by the polymer matrix.

Chapter 4 mentions the design of helical inorganic crystals in macroscopic scales. The helical morphologies emerged from nonsymmetrical crystals through the assembly of tilted unit crystals under diffusion-limited conditions. The twisted twins of the tilted unit crystal made up the backbone of helical morphologies. Moreover, the macroscopic chirality in helical crystals was precisely tuned with addition of chiral amino acids through stereochemical molecular recognition.

Chapter 5 describes the hierarchically organized architectures from nanoscopic to macroscopic scales. The exquisite association of crystals and polymers generated the hierarchically organized architecture consisting of nanocrystals 20 nm in size. The specific interaction between crystals and polymer and the diffusion-controlled condition played important roles for the hierarchical crystal design.

Chapter 6 focuses on the structural analogies of real biominerals and biomimetic architectures, as shown in chapters 2 and 5, and the potential for the host materials of dye molecules. Various dye molecules were introduced in the nanoscopic molecular storage generated from nanocrystals and polymers.

Chapter 7 summarizes the results and discussion of this study and then mentions the prospects of biomimetic approach for crystal design.