## Principles and Results Related to Biomimetic Crystal Design

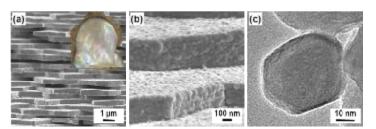
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An ultimate goal in our research is to synthesize highly functional materials through controlled crystal growth in solutions under mild conditions without any special equipment. Biominerals such as seashells, eggshells, and teeth are functional inorganic/organic composites consisting of abundant minerals formed under mild conditions (Figure 1).[1] Their structures and formation processes are good models for materials chemists. The controlled hierarchical structures lead to the emergence of functions that are not conceivable from each component such as calcium carbonate and biological polymers. The formation process, namely biomineralization, inspires researchers to develop mild condition routes for synthesis of designed crystals. In biomineralization, organic molecules such as proteins and peptides play essential roles for the construction of hierarchically organized inorganic/organic

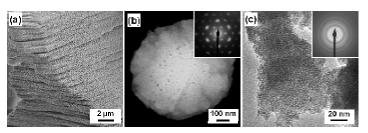
composites. A large amount of previous works have partially clarified the hierarchical structures and the related organic macromolecules in biominerals. However, we cannot synthesize replicas of biominerals in the present technology.

In biomimetic crystal design,



**Figure 1.** Hierarchically organized structures of nacreous layer, as an example of biominerals.[2a,b]

a wide variety of organic molecules play multiple roles for the control of crystal growth and the formation of composite structures through appropriate interactions. Biomimetic crystal design has been extensively studied by researchers in materials chemistry since 1990s. However, the research area is now developing. In recent years, biomimetic and bio-inspired materials chemistry have attracted much interest in the world. A number of research projects related to biomineralization and biomimetics are proceeding. The special issues have been published in journals related to chemistry and materials science. In our research area, the term 'biomimetic' represents mimicking structures, formation processes, and functions of biominerals. Our recent challenges are listed as follows: 1) Can we expand the approaches to a broad range of materials science?, 2) Can we create functional materials and devices?, 3) Can we alternate the approach to conventional processes and current practical materials? In the presentation, I will talk about our recent approaches related to biomimetic crystal design in the following the introduction.[2–4] Our research group has found the overlooked nanostructures of CaCO<sub>3</sub>-based biominerals such as a nacreous



**Figure 2.** Hierarchically organized materials synthesized through biomimetic crystal design.[2–4]

layer and a sea urchin spine (Figure 1). Based on the results, the biominerals can be interpreted as hierarchically organized inorganic/organic composites from nanoscopic to macroscopic scales.[2] The hierarchical structures of biominerals themselves can be used for the synthesis and morphogenesis of other functional organic materials. The similar hierarchically organized materials can be synthesized by using organic molecules under mild conditions (Figure 2).[3] We have studied biomimetic crystal design of metal oxide nanostructures through an approach inspired by microbial mineralization of manganese and iron oxides in nature.[4] In this way, biomimetic crystal design has been developed in recent years. The more precise control of the synthetic processes and the resultant structures are required for the further development of biomimetic crystal design. In addition, our next challenge is focused on the emergence of functions based on biomimetic crystal design.

## References

[1] Key reviews: a) S. Mann, Nature 1988, 332, 119; b) L. Addadi, S. Weiner, Angew. Chem. Int. Ed. Engl. 1992, 31, 153; b) S. Mann, Nature 1993, 365, 499; c) S. Mann, Biomineralization Principles and Concepts in Bioinorganic Materials Chemistry (Eds. R.G. Compton, S.G. Davies, and J. Evans), Oxford University Press, Oxford, 2001; d) Handbook of Biomineralization (Eds.: E. Bäuerlein, P. Behrens, M. Epple), Wiley-VCH, Weinheim2007; e) T. Kato, Adv. Mater. 2000, 12, 1543; f) T. Kato, A. Sugawara, N. Hosoda, Adv. Mater. 2002, 14, 869; g) S.-H. Yu, H. Cölfen, J. Mater. Chem. 2004, 14, 2124; h) H. Imai, Y. Oaki, A. Kotachi, Bull. Chem. Soc. Jpn. 2006, 79, 1834; i) A.-W. Xu, Y. Ma, H. Cölfen, J. Mater. Chem. 2007, 17, 415; j) F. C. Meldrum, H. Cölfen, Chem. Rev. 2008, 108, 4332; k) N. A. J. M. Sommerdijk, G. de With, Chem. Rev. 2008, 108, 4499; l) S. Mann, Nat. Mater. 2009, 8, 781; m) T. Kato, T. Sakamoto, T. Nishimura, MRS Bull. 2010, 35, 127; n) H. Imai, Y. Oaki, MRS Bull. 2010, 35, 138.

[2] Nanostructures of biominerals: a) Y. Oaki, H. Imai, *Angew. Chem. Int. Ed.* **2005**, *44*, 6571; b) Y. Oaki, A. Kotachi, T. Miura, H. Imai, *Adv. Funct. Mater.* **2006**, *16*, 1633; c) Y. Oaki, H. Imai, *Small* **2006**, *2*, 66.

[3] Biomimetic crystal design of hierarchical architectures: a) Y. Oaki, H. Imai, *Cryst. Growth Des.* 2003, *3*, 711; b) Y. Oaki, H. Imai, *J. Am. Chem. Soc.* 2004, *126*, 9271; c) Y. Oaki, H. Imai, *Adv. Funct. Mater.* 2005, *15*, 1407; d) Y. Oaki, H. Imai, *Chem. Commun.* 2005, 6011; e) Y. Oaki, S. Hayashi, H. Imai, *Chem. Commun.* 2007, 2841; f) Y. Oaki, S. Kajiyama, T. Nishimura, H. Imai, T. Kato, *dv. Mater.* 2008, *20*, 3633; g) Y. Oaki, T. Anzai, H. Imai, *Adv. Funct. Mater.* 2010, *20*, 4127.

[4] Biomimetic crystal design of metal oxide nanomaterials: a) Y. Oaki, H. ImaiAdv. Mater. 2006, 18, 1807; b) Y. Oaki, H. Imai, Angew. Chem. Int. Ed. 2007, 46, 4951; c) Y. Oaki, H. Imai, Chem. Eur. J. 2007, 13, 8564; d) Y. Oaki, H. Imai, J. Mater. Chem. 2007, 17, 316; e) Y. Oaki, S. Kajiyama, T. Nishimura, T. Kato, J. Mater. Chem. 2008, 18, 4140; f) K. Sakaushi, Y. Oaki, H. Uchiyama, E. Hosono, H. Zhou, H. Imai, Nanoscale 2010, 2, 2424; g) K. Sakaushi, Y. Oaki, H. Uchiyama, E. Hosono, H. Zhou, H. Imai, Constraint 2010, 6, 776; h) Y. Oaki, H. Ohno, T. Kato, Nanoscale 2010, 2, 2362; i) M. Oba, Y. Oaki, H. Imai, Adv. Funct. Mater. 2010, 20, 4279.