2011 JAFOE Symposium
Session: Bioinspired Materials

June 7, 2011

Principles and Results Related to Biomimetic Crystal Design

Synthetic

Biogenic

OAKI Yuya

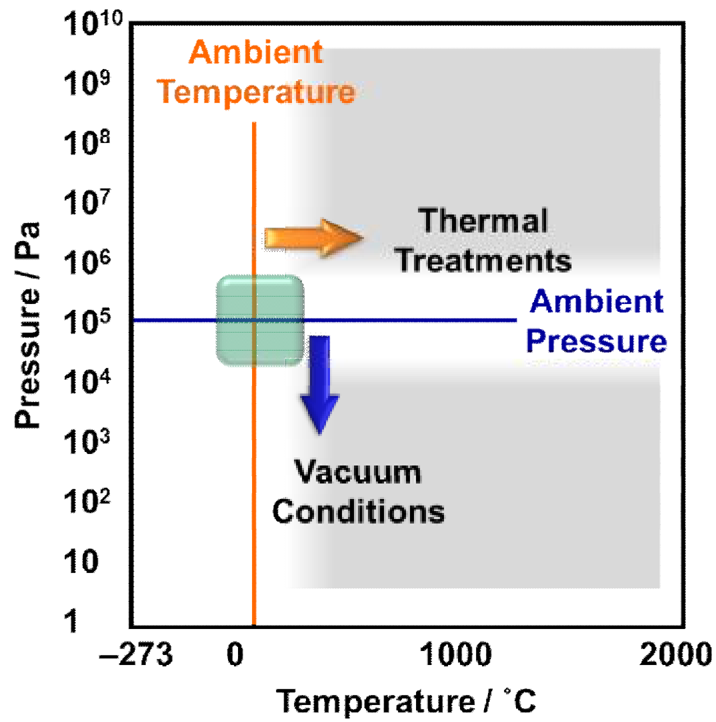
Dept. of Applied Chemistry, Keio University

Recent Materials Science

Development of Highly Functional Materials

Minimum Energy Consumption

Minimum Resource Consumption



Mottainai (もったいない)

Avoid Wastes!

What can materials scientists do?

Learning from Nature

What is biomimetic in materials science?

Models for Materials Science in Nature

Organisms

Minerals

Biological Systems

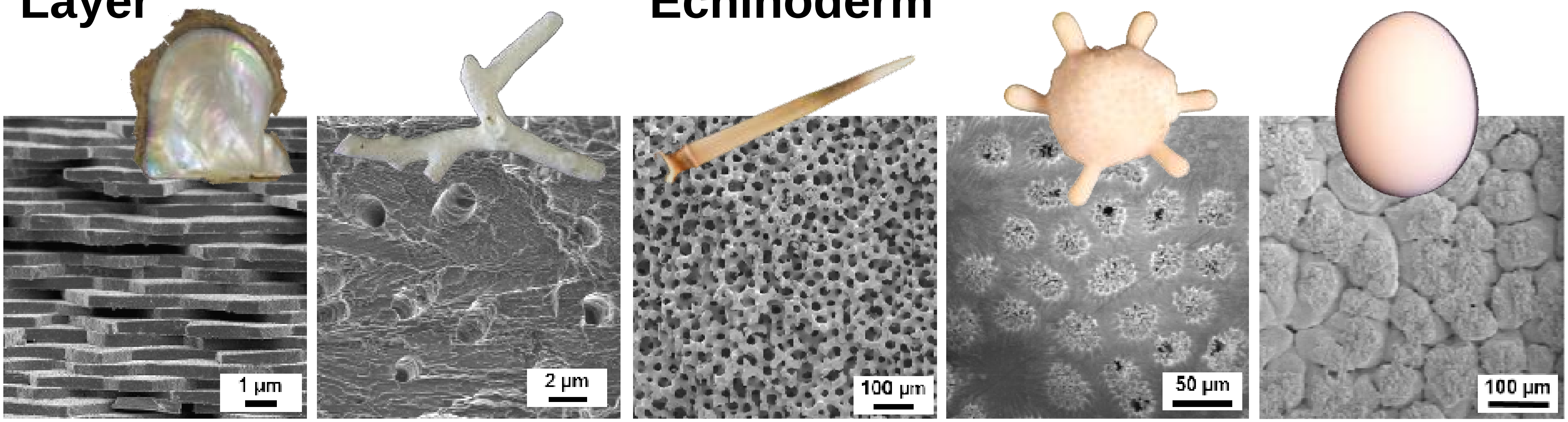
Biological Functions

Learning   Mimetic   Application

Development of Advanced Functional Materials in Harmony with Environment

What is biomimetic crystal design?

Nacreous Layer | Coral | Skeletal of Echinoderm | Foraminifer | Eggshell



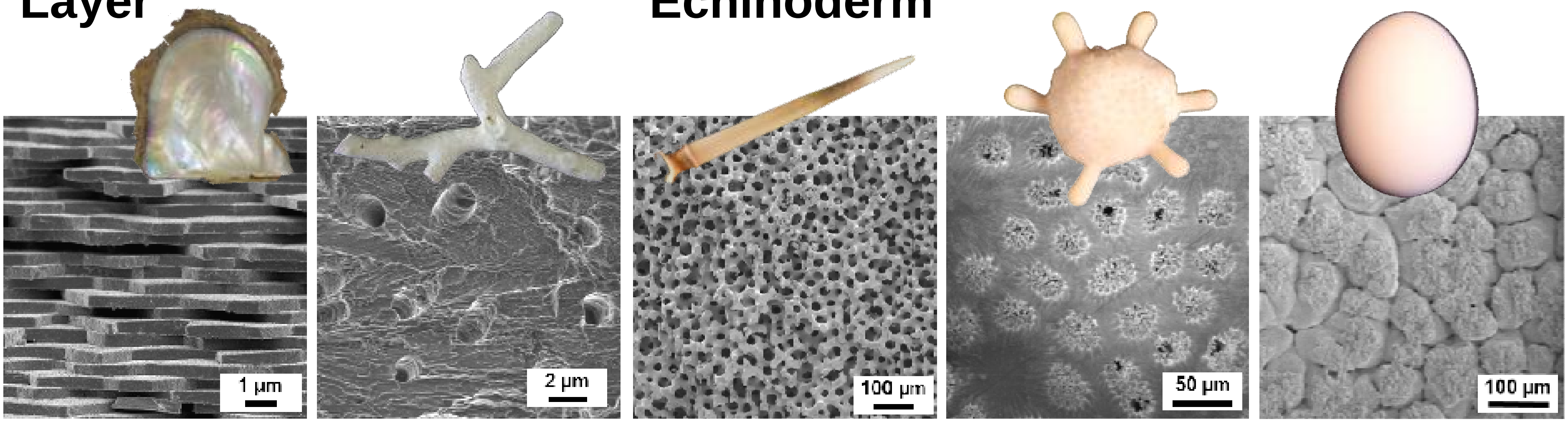
Biominerals

- Inorganic/Organic Composite
- Abundant Minerals
- Hierarchically Organized Structures
- Mild Condition Routes
- Reusable and Self-Repairable
- Highly Functional Materials

Good Models for Materials Science

What is biomimetic crystal design?

Nacreous Layer | Coral | Skeletal of Echinoderm | Foraminifer | Eggshell



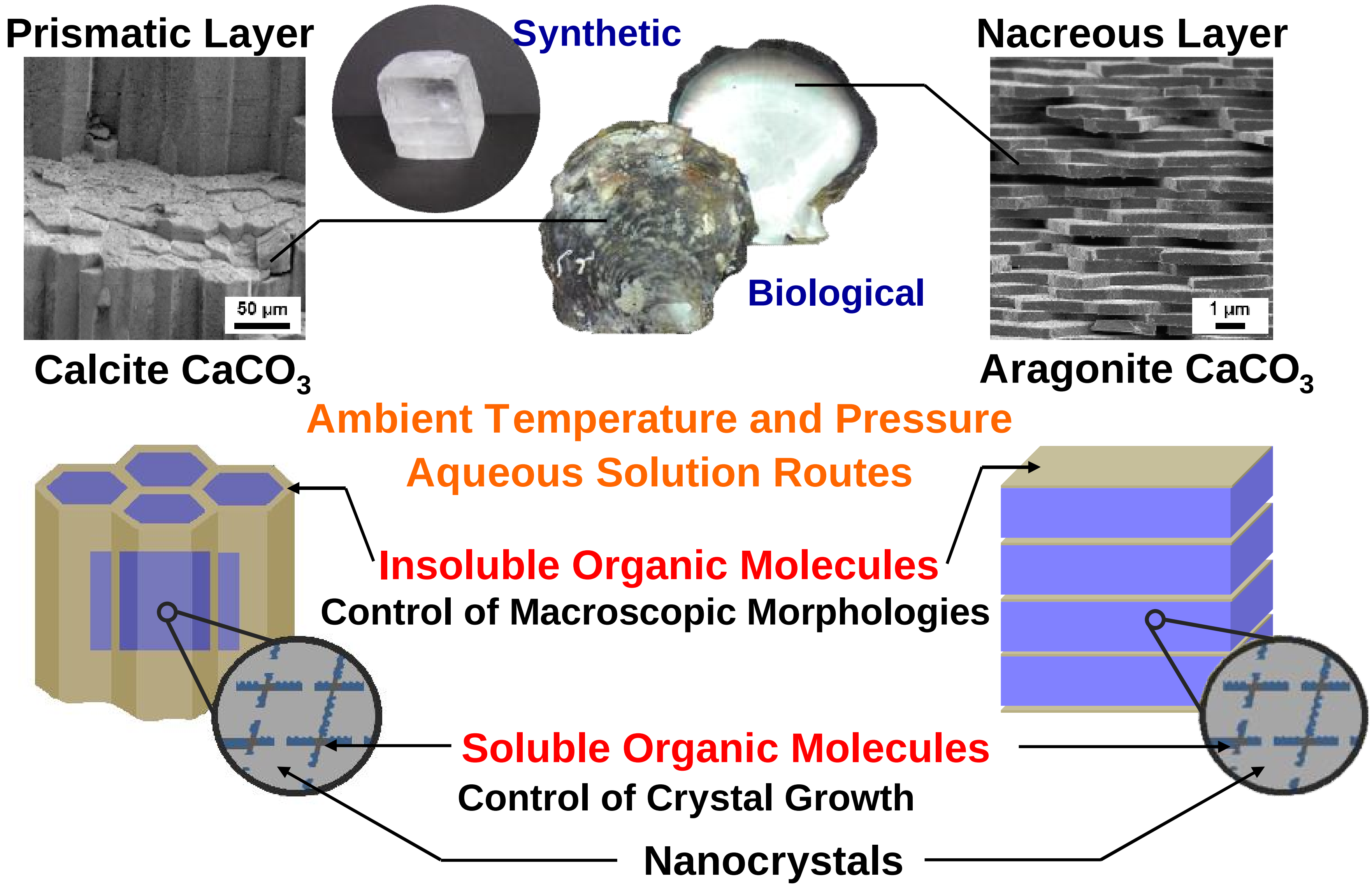
Biominerals

- Formation Processes
- Structures
- Functions

Learning | **Mimetic** | **Application**

➡ **Development of Advanced Functional Materials**

Principles and Concepts



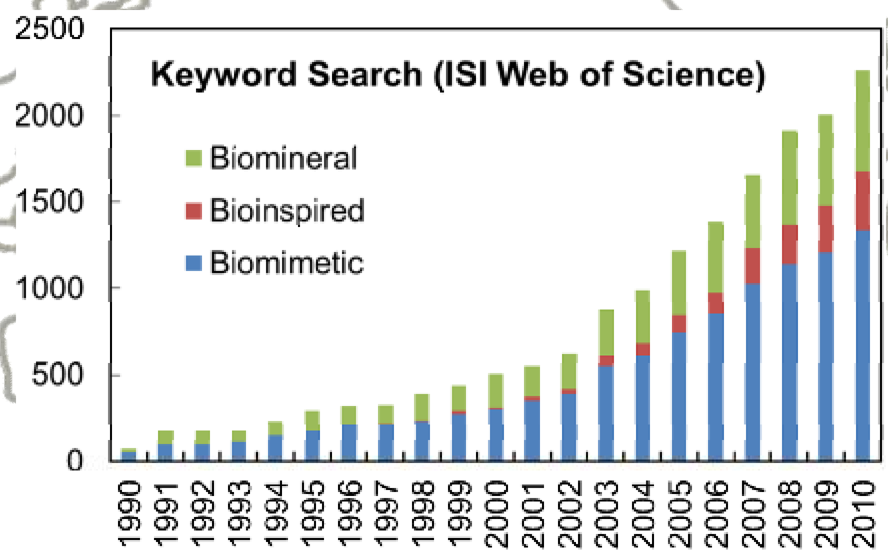
Recent Progress in World

S. Mann (Bristol)
F. C. Meldrum (Bristol)
M. Antonietti (MPI)
H. Cölfen (Konstanz)
N. Sommerdijik (Eindhoven)

S. H. Yu (USTC)
Q. Li (Peking)

J. Aizenberg (Harvard)
L. B. Gower (Florida)

L. Addadi (Weitzman)
S. Weiner (Weitzman)



Special Issues
2004 J. Mater. Chem.
2007 CrystEngComm
2009 Adv. Mater.

2008 Chem. Rev.
2010 MRS Bulletin

Development of Biomimetic Crystal Design

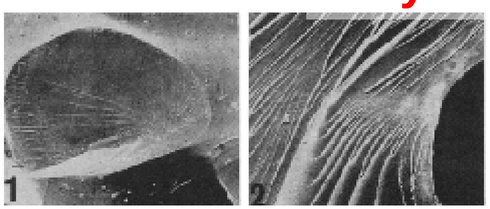
Biomineralization (1900~)

K. M. Towe,
***Science* 1967**

Echinoderm Calcite: Single Crystal or Polycrystalline Aggregate

Abstract. *Electron microscopy of natural and broken surfaces of echinoid skeletal plates reveals that the interior portions have the morphology of a single crystal, whereas the exterior is a polycrystalline aggregate with preferred orientation. These data help to resolve earlier contradictory x-ray and optical evidence.*

Crystal Structures



J. D. Currey *et al.*
***Nature* 1967**

Letters to Nature

Nature 214, 81-83 (1 April 1967) | doi:10.1038/214081a0

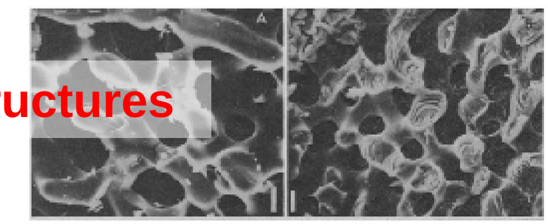
Absence of Organic Phase in Echinoderm Calcite

J. D. CURREY & DAVID NICHOLS

P. L. O'Neill,
***Science* 1981**

Polycrystalline Echinoderm Calcite and Its Fracture Mechanics

Abstract. *Polycrystalline calcite was revealed by scanning electron microscopy of fractured skeletal ossicles of the sea star* Echinaster spinulosus *(Echinodermata, Asteroidea). Whisker-like calcite crystals were observed in specimens that were loaded in stress relaxation before being fractured; rapidly broken surfaces were smooth and glassy. The crystallites were 1300 angstroms wide and at least 3500 angstroms long and were packed together in lamellae. The lamellae were wound into spirals that formed the trabecular bars. All the crystallites in an ossicle appear to be aligned in the same direction. Geometric considerations indicate that the requirement for packing the crystallites smoothly may explain the high magnesium ion concentration of echinoderm calcite.*



L. Addadi *et al.*
***Science* 2004**

Formation Mechanisms

Sea Urchin Spine Calcite Forms via a Transient Amorphous Calcium Carbonate Phase

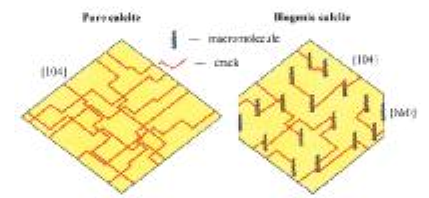
Yael Politi,[1] Talmon Arad,[2] Eugenia Klein,[2] Steve Weiner,[1] Lia Addadi[1]*

The skeletons of adult echinoderms comprise large single crystals of calcite with smooth convoluted fenestrated morphologies, raising many questions about how they form. By using water etching, infrared spectroscopy, electron diffraction, and environmental scanning electron microscopy, we show that sea urchin spine regeneration proceeds via the initial deposition of amorphous

L. Addadi *et al.*
***Science* 1990**
J. Aizenberg *et al.*
***J. Mater. Chem.* 2004**

Intercalation of Sea Urchin Proteins in Calcite: Study of a Crystalline Composite Material

AMIR BERMAN, LIA ADDADI, ÅKE KVICK, LESLIE LEISEROWITZ, MITCH NELSON, STEPHEN WEINER



J. Aizenberg *et al.*
***J. Am Chem. Soc.* 1993**

	sea urchin spines	
	EDTA	HCl
[protein][a]	0.009	0.015
Asx	10.0	12.1
Thr	5.0	4.6
Ser	4.6	3.6
Glx	10.9	12.9
Pro	10.3	10.1
Gly	15.4	19.1
Ala	11.5	9.9
Cys	0.7	0.2
Val	5.8	4.3
Met	4.3	4.9
Ile	3.5	3.0
Leu	5.6	3.7
Tyr	[illegible]	2.7
Phe	3.8	3.6
Lys	[illegible]	[illegible]
His	2.0	1.2
Arg	3.4	2.9

Compositions of Amino Acids

Development of Biomimetic Crystal Design

From Biomineralization to Biomimetic Materials Chemistry (1990~)

S. Mann (UK) 1993

***Nature* 1988**

REVIEW ARTICLE

Molecular recognition in biomineralization

Stephen Mann

School of Chemistry, University of Bath, Bath BA2 7AY, UK

The deposition of precise arrays of inorganic crystals in many organisms involves controlled nucleation at interfaces between the crystals and substrate macromolecules. These inorganic-organic molecular

***Nature* 1993**

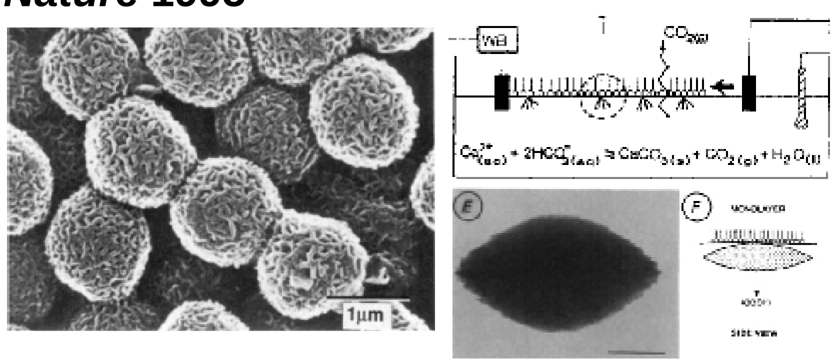
REVIEW ARTICLE

Molecular tectonics in biomineralization and biomimetic materials chemistry

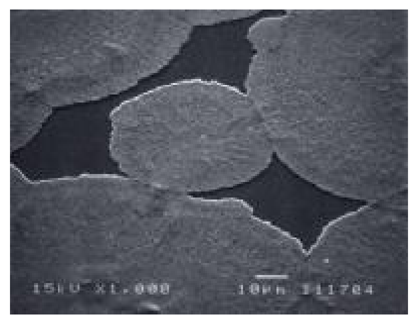
Stephen Mann

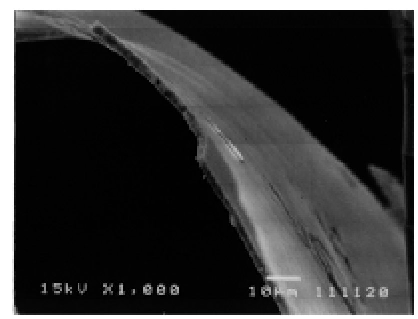
The systematic fabrication of advanced materials will require the construction of architectures over scales ranging from the molecular to the macroscopic. The basic constructional processes of biomineralization—supramolecular pre-organization, interfacial molecular recognition (templating) and cellular processing—can provide useful archetypes for molecular-scale building, or 'molecular tectonics', in inorganic materials chemistry.

***Nature* 1995**



T. Kato (Japan) 1998

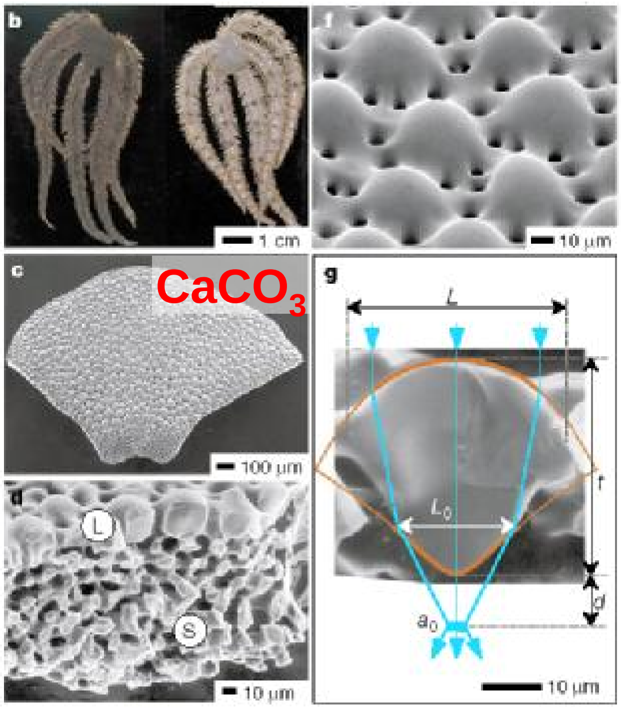


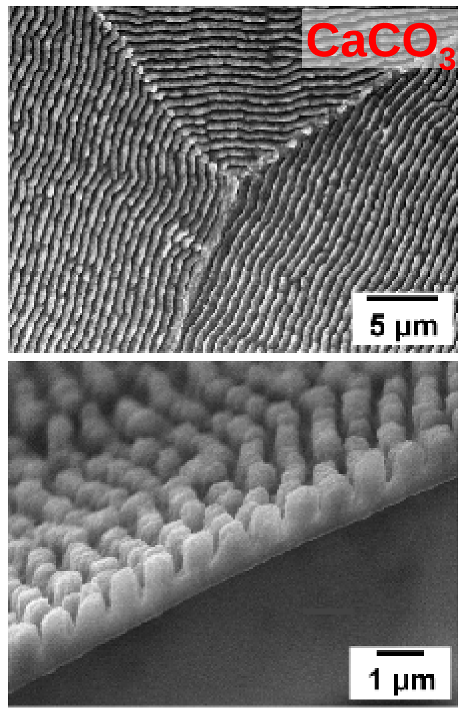


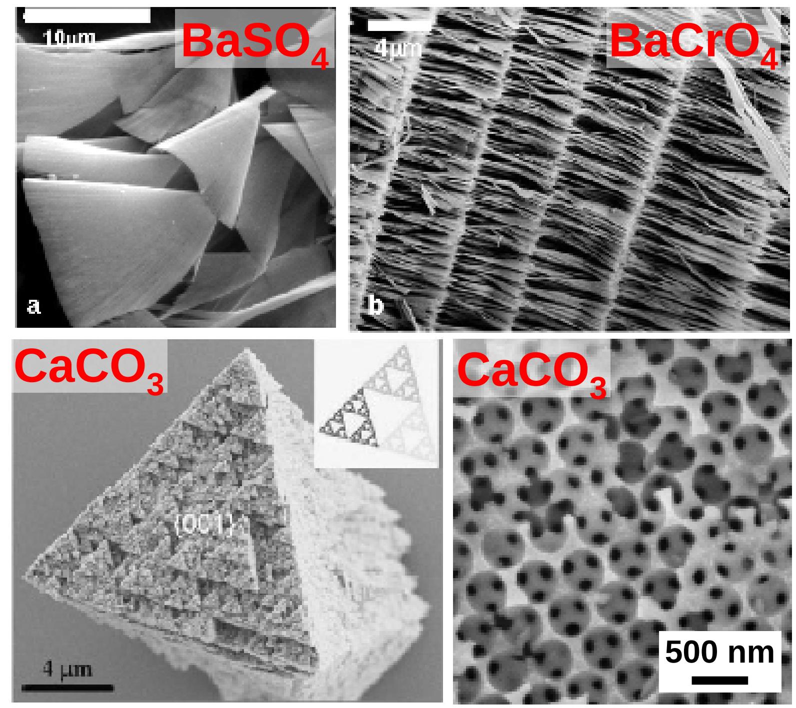
T. Kato *et al.*, *Supramol. Sci.*, 1998,
Adv. Mater., 2000, *Adv. Mater.*, 2002, *14*, 869.

Development of Biomimetic Crystal Design

Biomimetic Materials Chemistry (2000~)







J. Aizenberg

***Nature* *2001*, 412. 819.**

T. Kato

***Angew. Chem. Int. Ed.* 2006.**

M. Antonietti, H. Cölfen

S. H. Yu, Q. Li

***Nano Lett.* 2004.**

***Angew. Chem. Int. Ed.* 2008.**

***Adv. Mater.* 2009.**

Complex Morphologies

Biomimetic Crystal Design for Materials Science

~Recent Challenges in Technological Aspects~

1. **Can we expand the approach to synthesize a variety of compounds ?**

2. **Can we create functional materials and devices?**

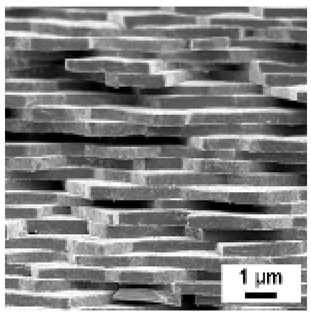
3. **Can we alternate the approach to conventional processes and current practical materials?**

Approaches to Biomimetic Crystal Design

Inorganic Salts

Nacreous Layer
Sea Urchin Spine

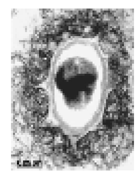
Calcium Carbonate

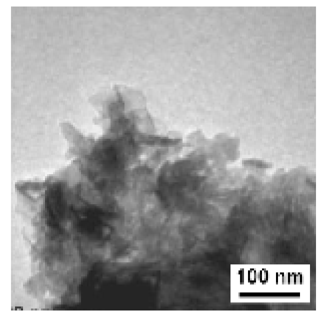


Metal Oxides

Metal-Oxidizing Bacteria

Manganese Oxides





Organic Crystals

Surface Skin of Fish

Guanine

Biominerals

- Formation Processes
- Structures
- Functions

Learning **Mimetic** **Application**

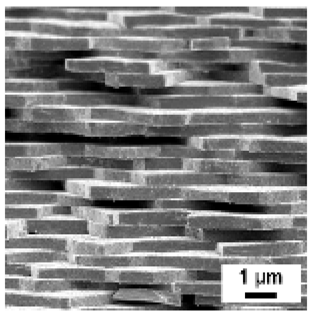
Development of A General Approach for Biomimetic Crystal Design

Approaches to Biomimetic Crystal Design

Inorganic Salts | **Metal Oxides** | **Organic Crystals**

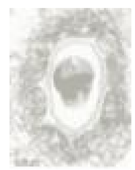
Nacreous Layer
Sea Urchin Spine

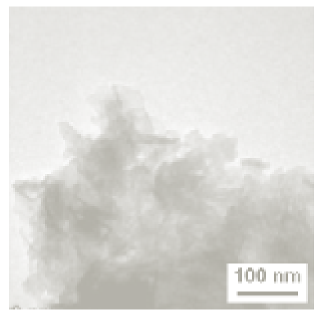
Calcium Carbonate



Metal-Oxidizing Bacteria

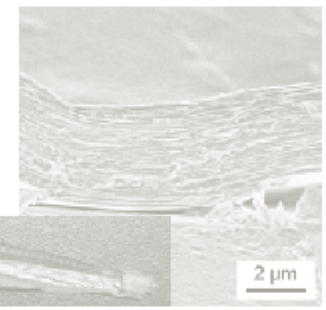
Manganese Oxides





Surface Skin of Fish

Guanine



Biominerals

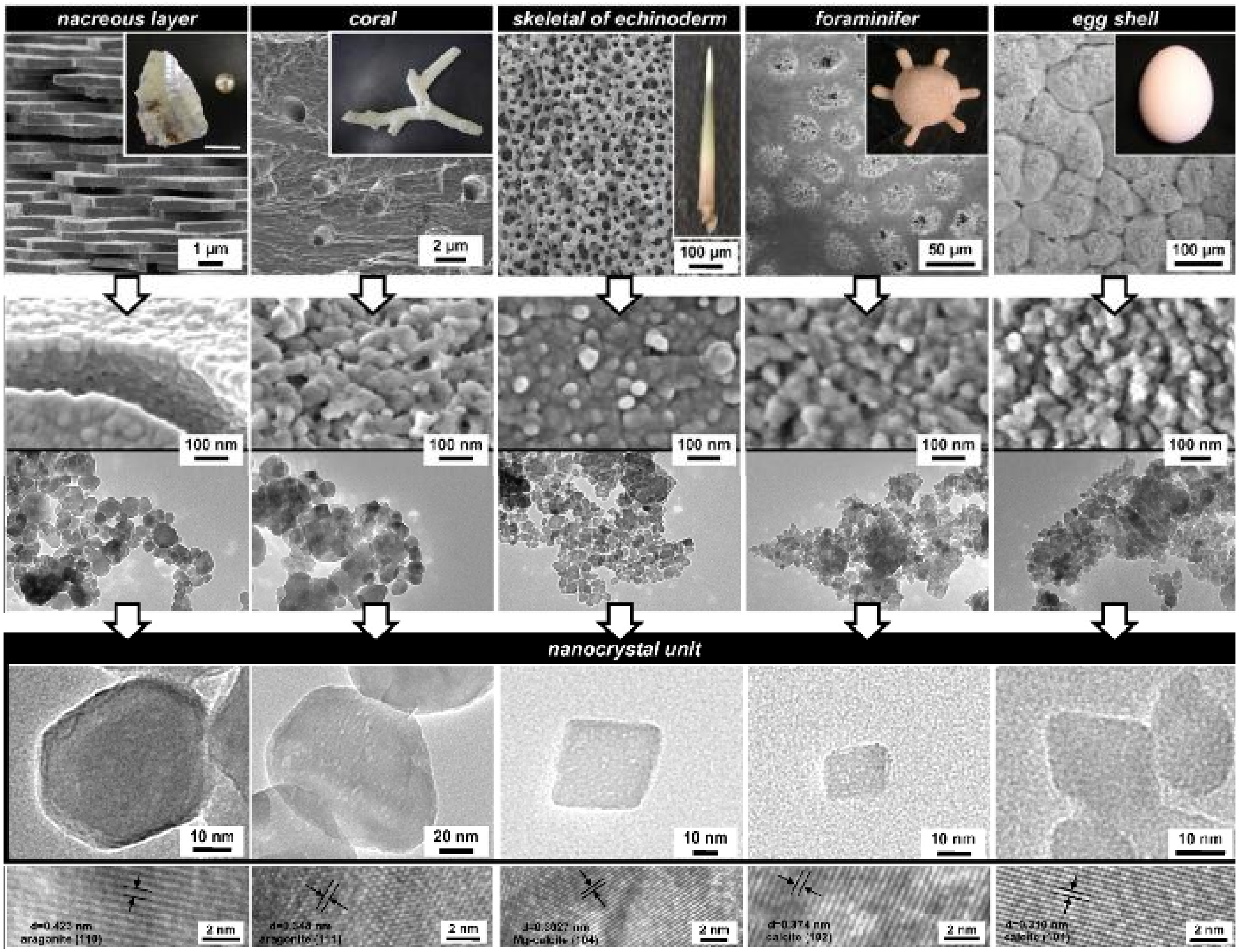
- Formation Processes
- Structures
- Functions

Learning **Mimetic** **Application**

➡ **Development of A General Approach for Biomimetic Crystal Design**

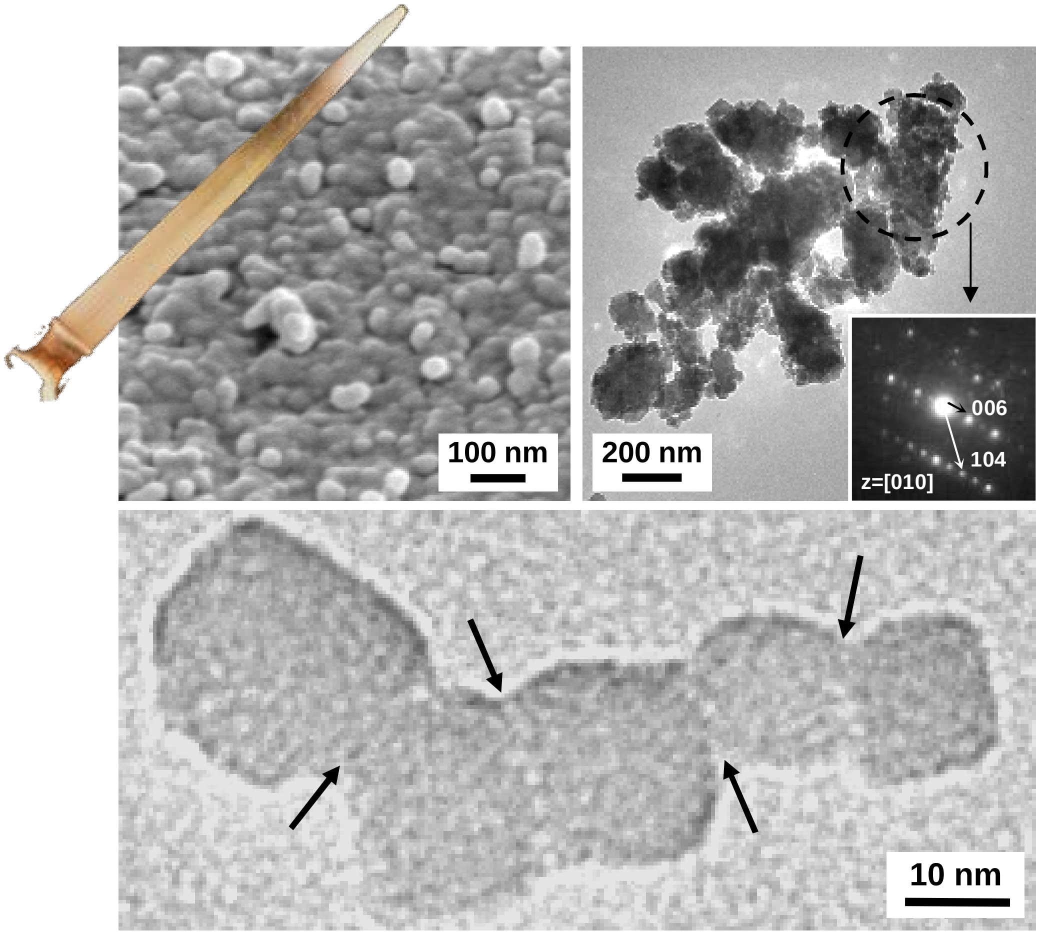
Strategies for Biological Crystal Design

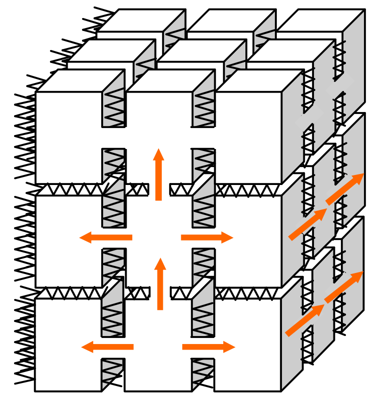
Single Crystal



Y. Oaki, H. Imai, *Angew. Chem. Int. Ed.* 2005, *44*, 6571.
Y. Oaki, A. Kotachi, T. Miura, H. Imai, *Adv. Funct. Mater.* 2006, *16*, 1633.

Strategies for Biological Crystal Design





Nanocrystals

Biological Polymers

Mineral Bridges

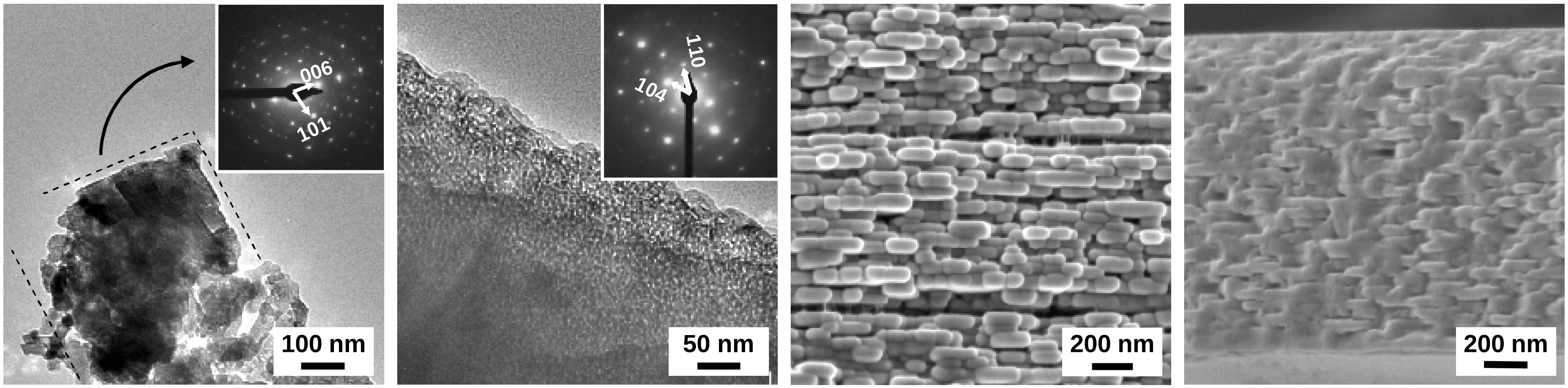
Oriented Structures

Mesocrystals

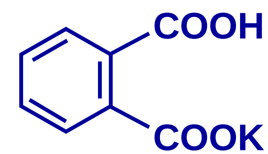
Y. Oaki, H. Imai, *Small* 2006, *2*, 66.

Y. Oaki, A. Kotachi, T. Miura, H. Imai, *Adv. Funct. Mater.* 2006, *16*, 1633.

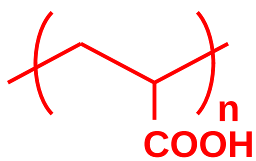
Biomimetic Crystal Design of Mesocrystals



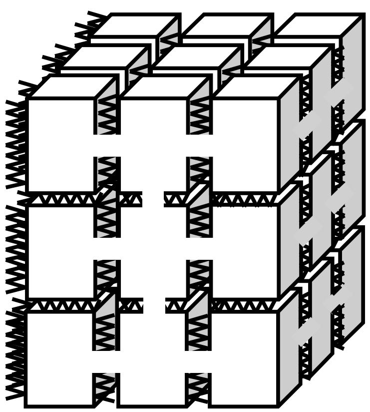
$CaCO_3$ $CaCO_3$ K_2SO_4



Biopolymers



PAA PAA PAA



Mesocrystals

Y. Oaki, H. Imai, *Adv. Funct. Mater.* 2005, *15*, 1407.

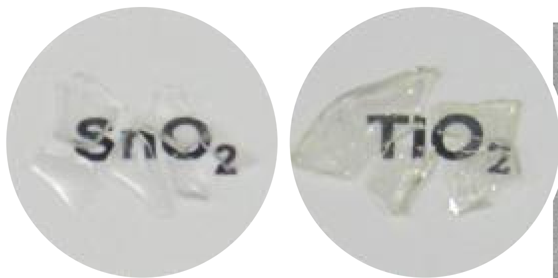
Y. Oaki, H. Imai, *Chem. Commun.* 2005, 6011.

Y. Oaki, A. Kotachi, T. Miura, H. Imai, *Adv. Funct. Mater.* 2006, *16*, 1633.

M. Kijima, Y. Oaki, H. Imai, *Chem. Eur. J.* 2011, *17*, 2828.

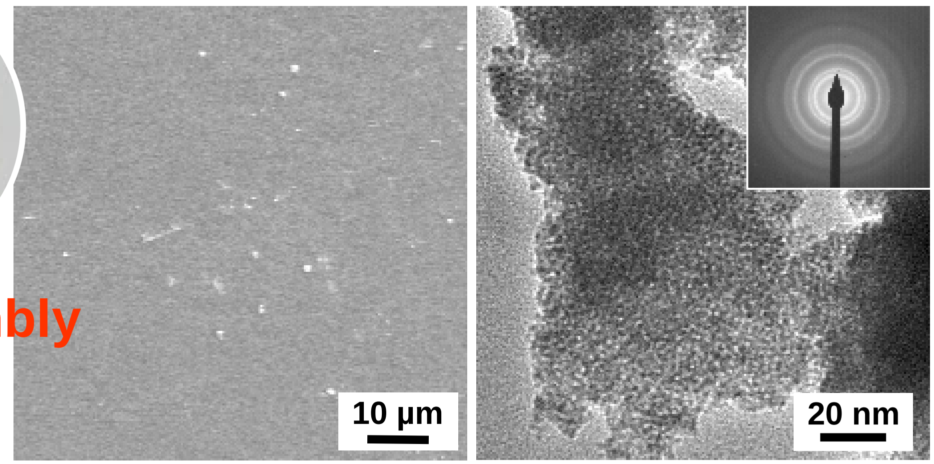
Applications of Biomimetic Crystal Design

SnO_2, TiO_2



Glass-Like
Transparent
Objects

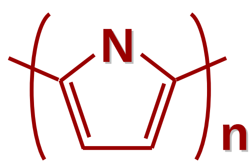
Homogeneous Assembly
of Nanocrystals



Y. Oaki, T. Anzai, H. Imai, *Adv. Funct. Mater.* 2010, *20*, 4127.

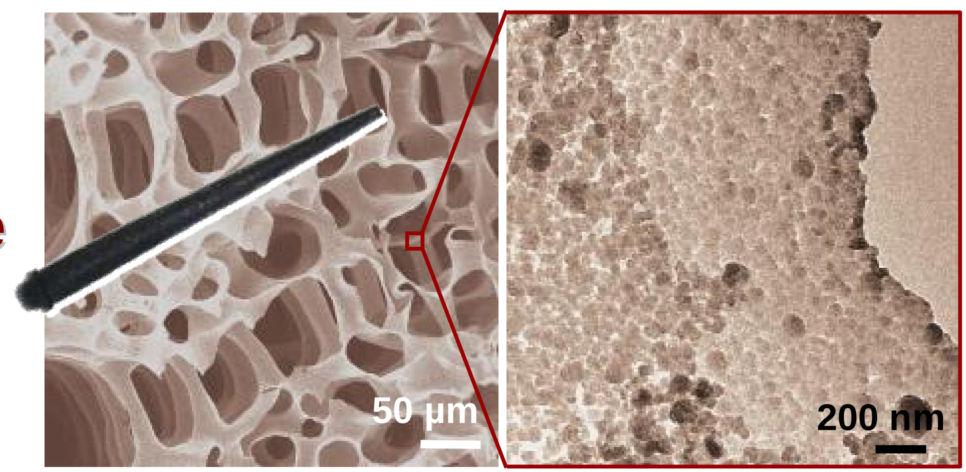
$CaCO_3$

Exoskeleton of
Sea Urchin Spine



Polypyrrole

Hierarchical
Architecture



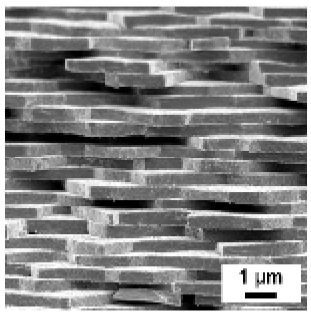
Y. Oaki, M. Kijima, H. Imai, *J. Am. Chem. Soc.* 2011, in press.

Approaches to Biomimetic Crystal Design

Inorganic Salts

Nacreous Layer
Sea Urchin Spine

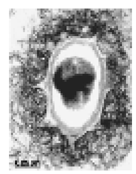
Calcium Carbonate

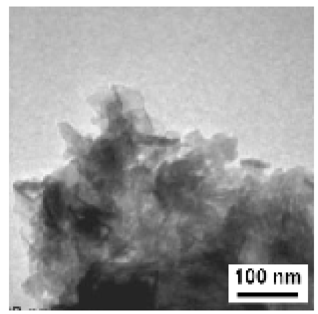


Metal Oxides

Metal-Oxidizing Bacteria

Manganese Oxides

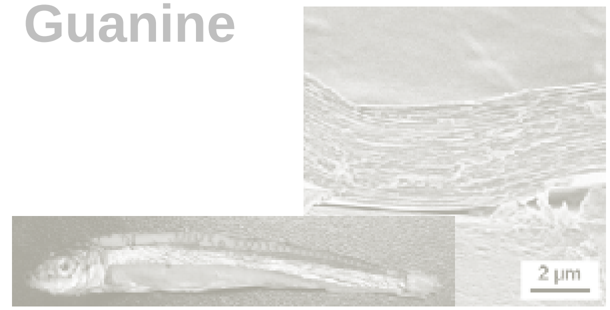




Organic Crystals

Surface Skin of Fish

Guanine



Biominerals

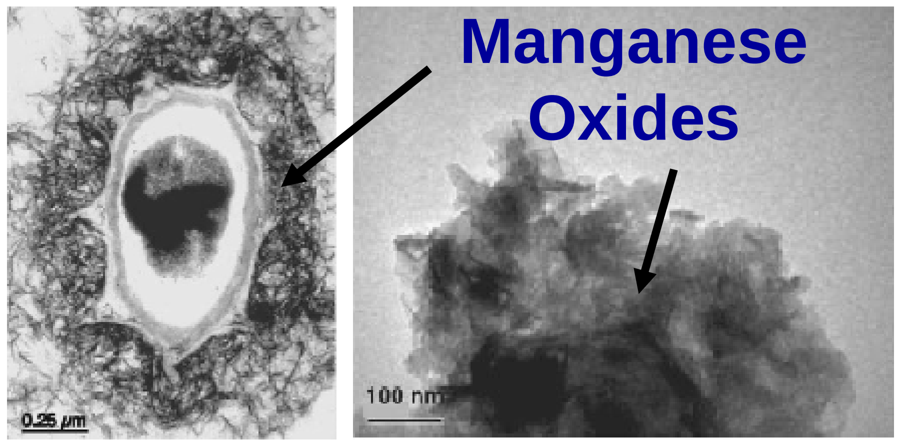
• Formation Processes • Structures • Functions

Learning Mimetic Application

Development of A General Approach for Biomimetic Crystal Design

Strategies for Biological Crystal Design

Manganese Oxidizing Bacteria



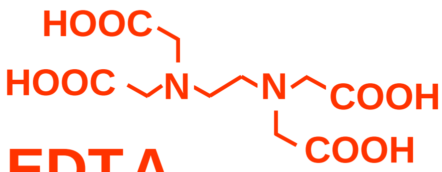
B. M. Tebo, S. M. Webb *et al., Annu. Rev. Earth Planet.* Sci 2004, *32*, 287.
***Trends Microbiol.* 2005, *13*, 421.**

- **Aqueous Solution Routes**
- **Nanostructures**
- **Controlled Oxidation States**
- **Enzyme-Mediated Syntheses**

Good Models for Materials Science

Biomimetic Crystal Design of Metal Oxides

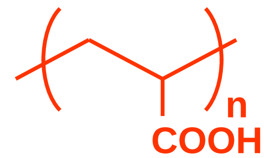
Enzyme-Mediated Synthesis → Chelation-Mediated Synthesis



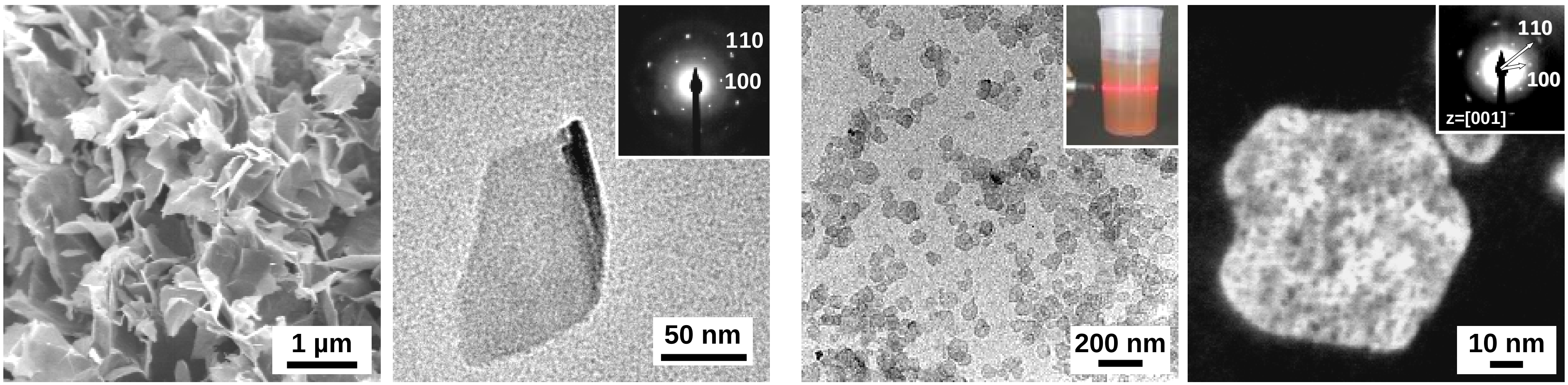
EDTA

$Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$

($Mn^{III,IV}$: birnessite)

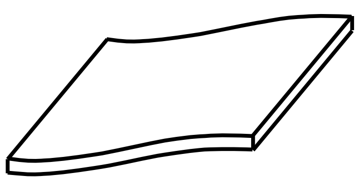


PAA



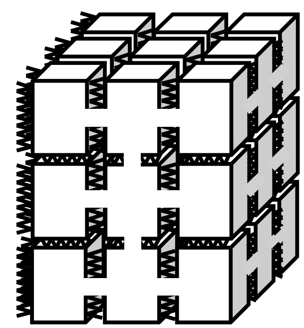
Nanosheets

- Thickness: 10 nm
- Size: 0.2 ~ 2 µm



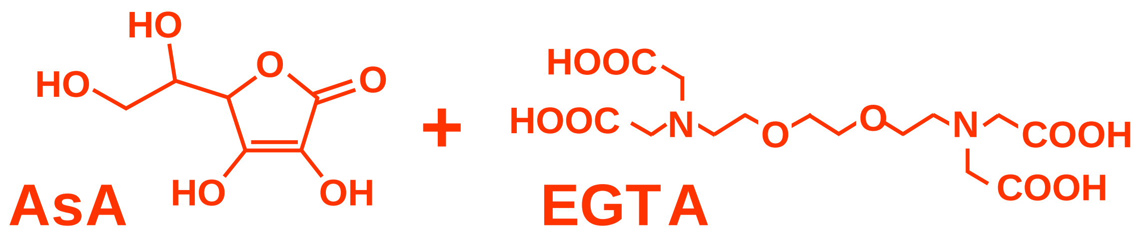
Mesocrystals

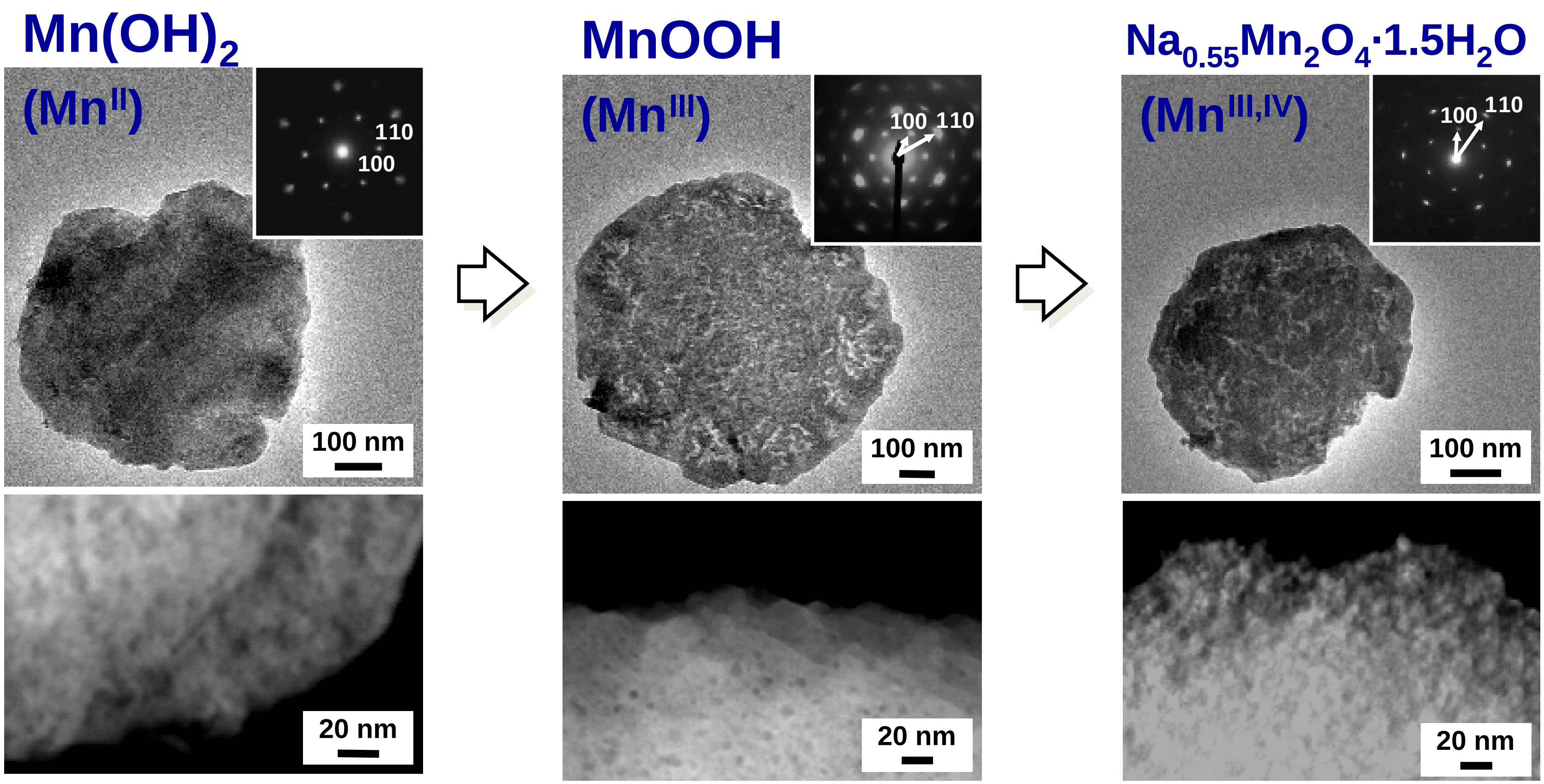
- Nanoflake: 100 nm
- Nanocrystal: 2 nm



Y. Oaki, H. Imai, *Angew. Chem. Int. Ed.* 2007, *46*, 4951. Y. Oaki, H. Imai, *J. Mater. Chem.* 2007, *17*, 316.

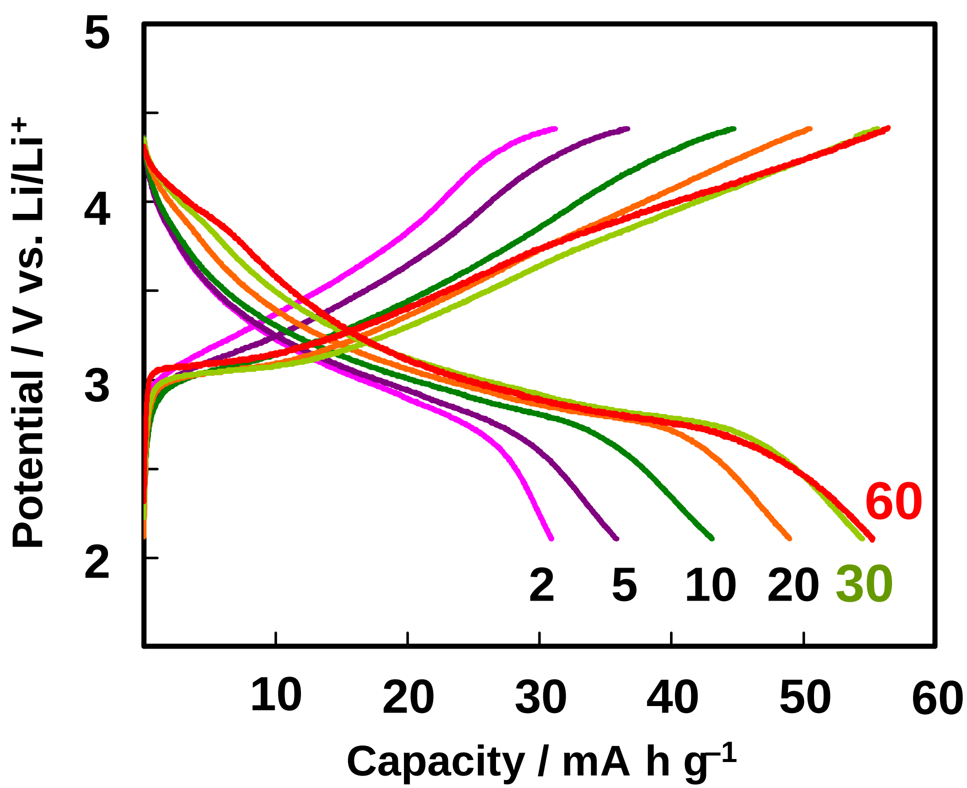
Biomimetic Crystal Design of Metal Oxides





M. Oba, Y. Oaki, H. Imai, *Adv. Funct. Mater.* 2010, *20*, 4279.

Application to Electrode Materials

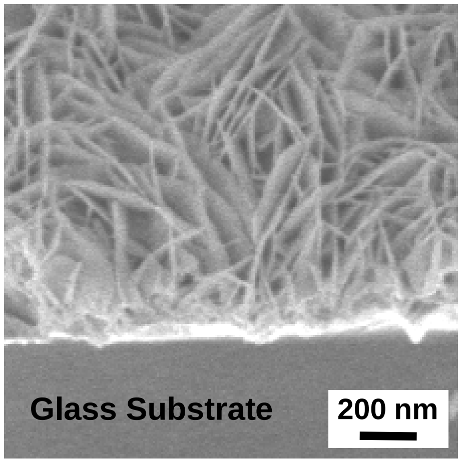


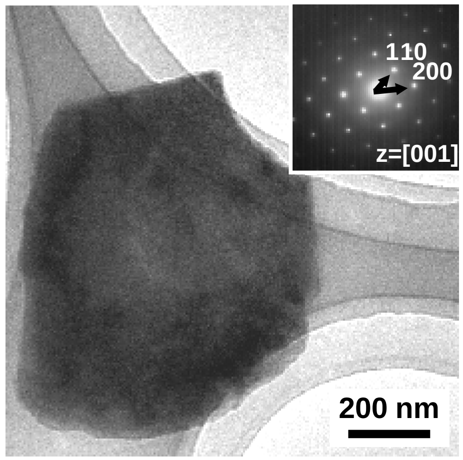
➩ **A Cathode Material of Lithium Ion Battery with Charge-Discharge Cycle Stability**

M. Oba, Y. Oaki, H. Imai, *Adv. Funct. Mater.* 2010, *20*,

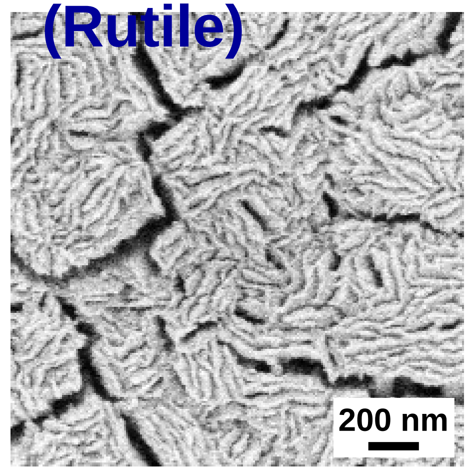
Biomimetic Crystal Design of Metal Oxides

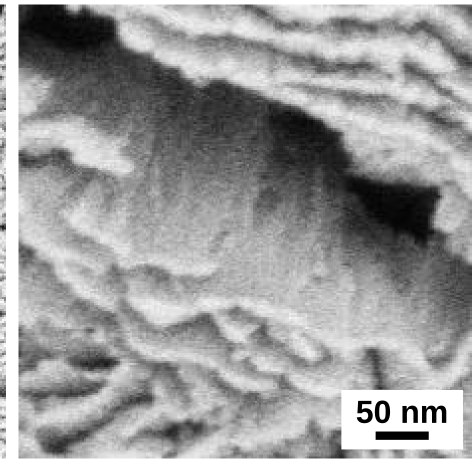
SnO (Sn^{II})



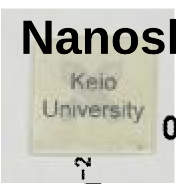


TiO_2 (Rutile)

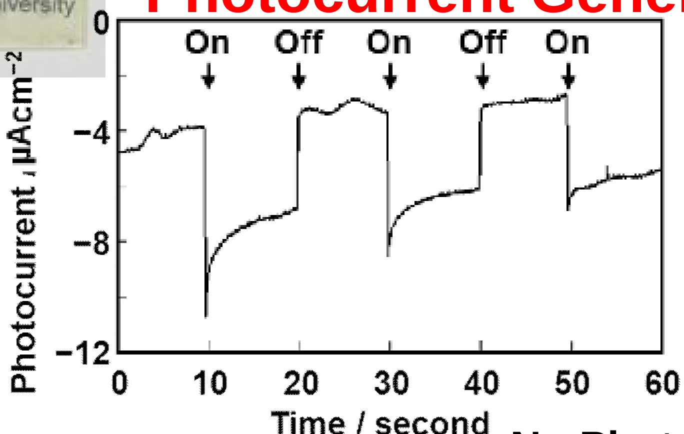




Nanosheets



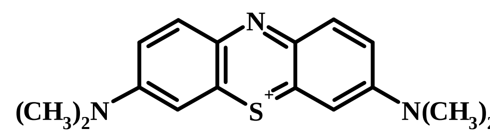
Photocurrent Generation



Bulk

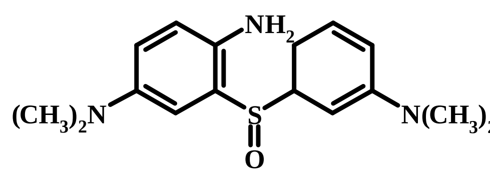
No Photocurrent

Photocatalytic Degradation

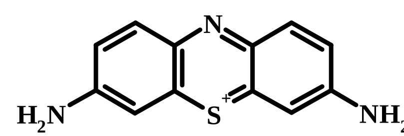


Reaction Selectivity

Reduction



Oxidation



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