RESEARCH

1. *MULTIFUNCTIONAL INORGANIC BIOMATERIALS: LESSONS FROM BIOMINERALIZATION*

1.1. "Nanotechnology" of biologically formed inorganic crystalline materials

Biological systems provide numerous examples of elaborate crystalline materials with exceptional nanostructural, mechanical, optical and magnetic properties (Fig.1). Our studies show that inorganic crystallization is finely tuned at the molecular level by organized assemblies of specialized macromolecules. The details of how this is achieved are still largely "terra incognita". *The general objective of our research in this sub-area is to study the exceptional crystalline properties of biominerals, to characterize biomacromolecules that control their formation and to search for fundamental mechanisms and common strategies used by organisms to manipulate inorganic crystalline materials.*

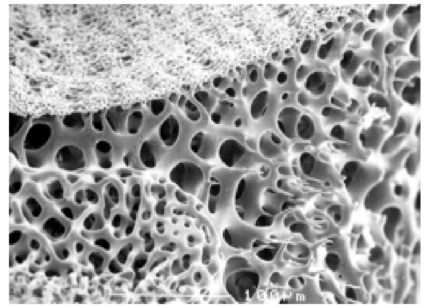

Fig.1. Echinoderm skeleton. The entire elaborate micro/nano-mesh is a single calcite crystal.

<u>Selected publications</u>:

"Interactions of Various Skeletal Intracrystalline Components with Calcite Crystals", S. Albeck, <u>J. Aizenberg</u>, L. Addadi, S. Weiner, *J. Am. Chem. Soc.*, **1993**, *115*, 25, 11691-11697.

"Crystal - Protein Interactions Studied by Overgrowth of Calcite on Biogenic Skeletal Elements", <u>J. Aizenberg</u>, S. Albeck, S. Weiner, L. Addadi, *J. Cryst. Growth*, **1994**, *142*, 156-164.

"Biologically-Induced Reduction in Symmetry: A Study of Crystal Texture of Calcitic Sponge Spicules", <u>J. Aizenberg</u>, J. Hanson, T. F. Koetzle, L. Leiserowitz, S. Weiner, L. Addadi, *Chem. Eur. J.*, **1995**, *7*, 414-422.

"Stabilization of Amorphous Calcium Carbonate by Specialized Macromolecules in Biological and Synthetic Precipitates", <u>J. Aizenberg</u>, G. Lambert, L. Addadi, S. Weiner, *Adv. Mat.*, **1996**, *8*, 222-225.

"Control of Macromolecule Distribution within Synthetic and Biogenic Single Calcite Crystals", <u>J. Aizenberg</u>, J. Hanson, T. F. Koetzle, S. Weiner, L. Addadi, *J. Am. Chem. Soc.*, **1997**, *119*, 881-886.

"Factors Involved in the Formation of Amorphous and Crystalline Calcium Carbonate: A Study of an Ascidian Skeleton", <u>J. Aizenberg</u>, G. Lambert, S. Weiner, L. Addadi, *J. Am. Chem. Soc.*, **2002**, *124*, 32-39.

Fig.2. Microlens array in a brittlestar.

1.2. Biooptics

The most advanced optical designs made by humans are often primitive relative to the optical systems that have evolved in Nature. Aizenberg and colleagues have recently discovered two unique optical systems, whose hierarchical architecture and hybrid character offer outstanding optical properties. First system is the arrays of calcitic microlenses formed by brittlestars (Fig.2). These optically perfect biolenses are designed to minimize spherical aberration and birefringence, to optimize the light intensity and wavelength, to increase the focusing capability and to detect light from a particular direction. Second system is glass waveguides produced by a deep-sea sponge (Fig.3). The ongoing optical and chemical characterization of these optical fibers shows that they are remarkably similar (and in many ways superior) to their technological analogs and highlight the importance of the ambient temperature synthesis favored in nature. *The general objective of the research in this sub-area is to search for smart biological solutions in design, synthesis, materials and integration of complex (inorganic) optical systems; to characterize their optical properties and advantages; to study their structure, composition and the mechanisms of formation, and to apply this knowledge to the fabrication of novel, adaptive optical devices.*

Fig.3. Network of optical fibers in a glass sponge

Selected publications:

"Calcitic Microlenses as Part of the Photoreceptor System in Brittlestars", J. Aizenberg, A. Tkachenko, S. Weiner, L. Addadi, G. Hendler, *Nature*, **2001**, ***412***, 819-822.

"Fiber-Optical Features of a Glass Sponge", V. C. Sundar, A. D. Yablon, J. L. Grazul, M. Ilan, J. Aizenberg, *Nature*, **2003**, *424*, 899-900.

"Designing Efficient Microlens Arrays: Lessons from Nature", J. Aizenberg, G. Hendler, *J. Mater. Chem.,* **2004,** *14*, 2066-2072.

"Biological Glass Fibers: Correlation between Optical and Structural Properties", J. Aizenberg, V. C. Sundar, A. D. Yablon, J. C. Weaver, G. Chen, *Proc. Nat. Acad. Sci. USA*, **2004**, *101*, 3358-3363.

1.3. Mechanical and structural properties of mineralized tissues

The level of control that organisms exercise over the mechanical properties of structural inorganic biomaterials is unparalleled in modern mechanical engineering. Our studies suggest that these properties originate from a sophisticated structural design achieved by the interplay between inorganic minerals and organic biological macromolecules (Fig. 4). *This research is aimed at studying biological composite materials and understanding how biology arranges simple minerals into complex architectures.*

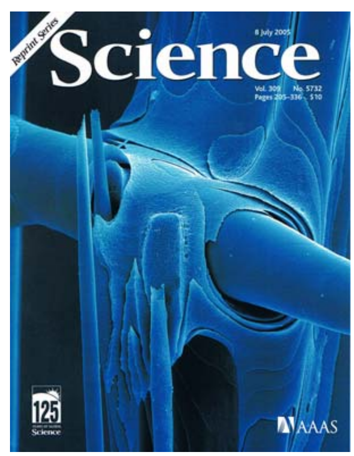

Fig.4. Laminated bioglass with interlayer organic glue

Selected publications:

"Skeleton of *Euplectella sp.*: Structural Hierarchy from the Nanoscale to the Macroscale", J. Aizenberg, J. C. Weaver, M. S. Thanawala, V. C. Sundar, D. E. Morse, P. Fratzl, *Science* **2005,** *309*, 275-278.

“Micromechanical Properties of Biological Silica in Skeletons of Deep-Sea Sponges”, A. Woesz, J. C. Weaver, M. Kazanci, Y. Dauphin, D. E. Morse, J. Aizenberg, P. Fratzl, *J. Mater. Res.*, **2006**, *21*, 2068-2078.

“Hierarchical Assembly of the Siliceous Skeletal Lattice of the Hexactinellid Sponge *Euplectella aspergillum*”, J. C. Weaver, J. Aizenberg, G. E. Fantner, D. Kisailus, A. Woesz, P. Allen, K. Fields, M. J. Porter, F. W. Zok, P. K. Hansma, P. Fratzl, D. E. Morse, *J. Struct. Biol*. **2007**, *158*, 93–106.

2. *BIO-INSPIRED MATERIALS SYNTHESIS*

2.1. Control of crystallization by organized organic assemblies

An important requirement in the fabrication of advanced inorganic materials – from ceramics to semiconductors – is control over crystallization. The ability to tune crystal properties of inorganic solids in a predictable and reproducible manner is attractive to materials scientists and chemical engineers seeking to optimize and/or exploit selective physicochemical features of crystalline materials. Based on the biomineralization strategies, I have developed new biomimetic, “bottom-up” approaches to the synthesis of ordered inorganic crystalline materials using specially tailored micropatterned organic templates (Fig.5) and controlled amorphous-to-crystalline transitions (Fig.6). We demonstrated that these methods provide an unprecedented level of control over crystallization process. *The general objective of multiple projects in this area is to further develop “bottom-up” crystallization strategies; to synthesize advanced crystalline and colloidal materials with desired crystallization pattern, crystallographic orientation, sizes, shapes, nanostructure, purities and stability, and to study and model molecular recognition processes at the organic/inorganic interface.*

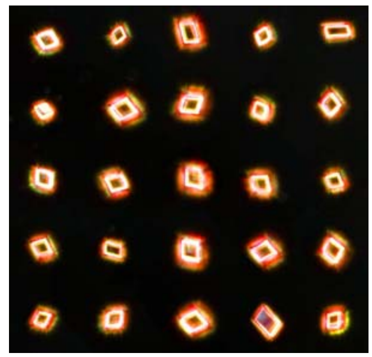

Fig.5. Array of uniform, oriented nanocrystals grown from an organically modified micropatterned substrate.

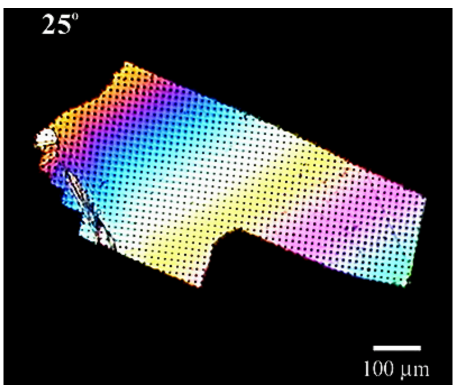

Fig.6. First example of a large macropatterned single crystal fabricated using “bottom-up” approach.

Selected publications:

“Oriented Growth of Calcite Controlled by Self-Assembled Monolayers of Functionalized Alkanethiols Supported on Gold and Silver”, J. Aizenberg, A. J. Black, G. M. Whitesides, *J. Am. Chem. Soc.*, **1999**, *121*, 4500-4509.

“Control of Nucleation by Patterned Self-Assembled Monolayers”, J. Aizenberg, A. J. Black, G. M. Whitesides, *Nature*, **1999**, *398*, 495-498.

“Patterned Colloidal Deposition Controlled by Electrostatic and Capillary Forces”, J. Aizenberg, P. V. Braun, P. Wiltzius, *Phys. Rev. Lett.*, **2000**, *84*, 2997-3000.

“Effect of Magnesium Ions on Oriented Growth of Calcite on Carboxylic Acid Functionalized Self-Assembled Monolayer”, Y.-J. Han, J. Aizenberg, *J. Am. Chem. Soc.*, **2003**, *125*, 4032-4033.

"Direct Fabrication of Large Micropatterned Single Crystals", J. Aizenberg, D. A. Muller, J. L. Grazul, D. R. Hamann, *Science*, **2003**, *299*, 1205-1208.

"Face-Selective Nucleation of Calcite on Self-Assembled Monolayers of Alkanethiols: Effect of the Parity of the Alkyl Chain", Y.-J. Han, J. Aizenberg, *Angew. Chem. Int. Ed.*, **2003**, *42*, 3668-3670.

"Crystallization in Patterns: A Bio-Inspired Approach", J. Aizenberg, *Adv. Mater.*, **2004**, *16*, 1295-1302.

"Template-Dependent Morphogenesis of Oriented Calcite Crystals in the Presence of Magnesium Ions", Y.-J. Han, L. M. Wysocky, M. Thanawala, T. Siegrist, J. Aizenberg, *Angew. Chem. Int. Ed.*, **2005,** *44*, 2386 - 2390.

"Patterned Growth of Large Oriented Organic Semiconductor Single Crystals on Self-Assembled Monolayer Templates", A. L. Briseno, Y.-J. Han, R. A. Penkala, H. Moon, A. J. Lovinger, C. Kloc, J. Aizenberg, Z. Bao, *J. Am. Chem. Soc*. **2005**, *127* (*35*), 12164-12165.

2.2. Tunable microlens arrays

In our effort to innovate communication technology by learning from nature, we have successfully developed synthetic routes to new, complex photonic structures, such as adjustable photolithographic masks and 3D biomimetic porous microlens arrays (Fig.7). *This synthetic and microfabrication effort is aimed at combining the advantageous optical and microfluidic features of natural optical systems and to create actively-switchable optical devices with wide tunability of optical properties (transmission, numerical aperture, wavelength selectivity,...).*

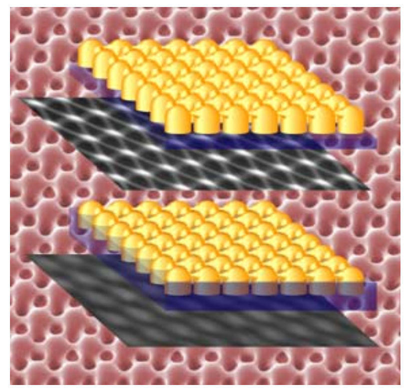

Fig.7. Synthetic microlenses with microfluidic system (note the similarity with the bioarray in Fig.2.

Selected publications:

"Functional Biomimetic Microlens Arrays With Integrated Pores", S. Yang, G. Chen, M. Megens, C. K. Ullal, Y.-J. Han, R. Rapaport, E. L. Thomas, J. Aizenberg, *Adv. Mater.*, **2005**, *17*, 435-438.

"Microlens Arrays with Integrated Pores as a Multipattern Photomask", S. Yang, C. K. Ullal, E. L. Thomas, G. Chen, J. Aizenberg, *Appl. Phys. Lett*. **2005**, *86*, 201121.

"Synthesis of Photoacid Crosslinkable Hydrogels for the Fabrication of Soft, Biomimetic Microlens Arrays" S. Yang, J. Ford, C. Ruengruglikit, Q. Huang, J. Aizenberg, *J. Mater. Chem.* **2005**, *15*, 4200-4202.

"Tunable Microfluidic Optical Devices with an Integrated Microlens Array", K.-S. Hong, J. Wang, A. Sharonov, D. Chandra, J. Aizenberg, S. Yang, *J. Micromech. Microeng.*, **2006**, *16*, 1660-1666.

3. *NEW NANOPATTERNING TECHNIQUES*

Underlying this project is the broad concept of biomimetics: that is, the use of self-assembly to fabricate chemically and topographically nanopatterned structures. We have developed a new nanopatterning technique that utilizes disorder in organically modified substrates. *The objective of this project is to study its application in various area-selective processes, including etching, selective chemical reactions, nanopatterned crystal growth (Fig.8), wetting and cell adhesion. Other novel nanopatterning techniques that utilize molecularly-designed substrates are developed.*

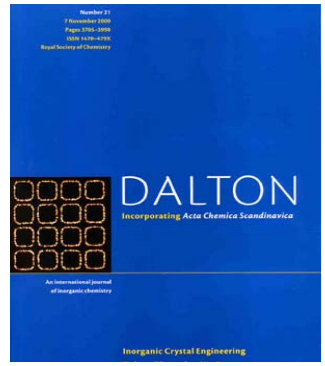

Fig.8. Using disorder to template patterned crystallization.

Selected publications:

“Controlling Local Disorder in Self-Assembled Monolayers by Patterning the Topography of their Metallic Supports”, J. Aizenberg, A. J. Black, G. M. Whitesides, *Nature*, **1998**, *394***,** 868-871.

“Patterning Disorder in Monolayer Resists for the Fabrication of sub-100-nm Structures in Silver, Gold, Silicon, and Aluminum”, A. J. Black, K. E. Paul, J. Aizenberg, G. M. Whitesides, *J. Am. Chem. Soc.*, **1999**, *121*, 8356-8365.

“Patterned Crystallisation on Self-Assembled Monolayers with Integrated Regions of Disorder”, J. Aizenberg**,** *J. Chem. Soc. Dalton Trans.*, **2000**, *21*, 3963-3968.

“Narrow Features in Metals at the Interfaces Between Different Etch Resists”, V. C. Sundar, J. Aizenberg, *Appl. Phys. Lett.*, **2003**, *83*, 2259-2261.

4. *ACTUATORS*

Aizenberg’s group designed new hybrid architectures, in which arrays of high-aspect-ratio silicon nanocolumns, either attached or free-standing, are embedded into a hydrogel film and are actuated into highly-controlled, complex microstructures. Our continuing research in this area addresses the optimization of the system, mechanical assessment of the actuation process, and the application of such actuation systems in actuators, controlled reversible pattern formation, microfluidics, reversible switching of the wetting behavior, tunable photonic structures, artificial muscles, and release systems.

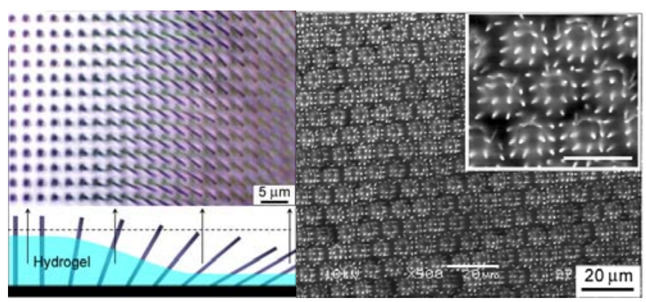

Fig.9. Actuation of the array of nanostructures.

Selected publications:

“Reversible Switching of Hydrogel-Actuated Nanostructures into Complex Micropatterns”, A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, J. Aizenberg, *Science* **2007,** *315*, 487-490.

5. *BIONANOINTERFACES*

We explore chemical functionalization of nanostructured surfaces and their use in various lab-on-a-chip biomedical, sensor and responsive materials applications.