

diffusional rewelding of the damage, thus providing the ultimate biomimetic property of self healing.

Thermodynamic compatibility of the pair of two-phase alloys requires a four-phase equilibrium at operating temperatures and a two-phase equilibrium during solution treatment. A preliminary thermodynamic feasibility analysis, including assessment of memory alloy stability requirements, was performed by a team of juniors in materials design class. Continued evaluation (38) has included a test of mechanical concepts that uses a TiNi-reinforced Sn alloy composite prototype to demonstrate both macroscopic strain reversal and the desired crack-clamping behavior (41). Precise multicomponent phase relations for the Fe-based system have been evaluated with diffusion couple experiments, and prototype steel composites are being fabricated.

The success of these initial designs suggests that the integration of computational materials science within a systems engineering framework offers a powerful new approach for the creation of superior materials that have sophisticated control of a multi-level dynamic structure, combined with reduced time and cost of materials development. These first steps herald a new synergy of the science and engineering of materials.

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# Molecular Manipulation of Microstructures: Biomaterials, Ceramics, and Semiconductors

Samuel I. Stupp\* and Paul V. Braun

Organic molecules can alter inorganic microstructures, offering a very powerful tool for the design of novel materials. In biological systems, this tool is often used to create microstructures in which the organic manipulators are a minority component. Three groups of materials—biomaterials, ceramics, and semiconductors—have been selected to illustrate this concept as used by nature and by synthetic laboratories exploring its potential in materials technology. In some of nature's biomaterials, macromolecules such as proteins, glycoproteins, and polysaccharides are used to control nucleation and growth of mineral phases and thus manipulate microstructure and physical properties. This concept has been used synthetically to generate apatite-based materials that can function as artificial bone in humans. Synthetic polymers and surfactants can also drastically change the morphology of ceramic particles, impart new functional properties, and provide new processing methods for the formation of useful objects. Interesting opportunities also exist in creating semiconducting materials in which molecular manipulators connect quantum dots or template cavities, which change their electronic properties and functionality.

The functionality of materials in macroscopic form is seldom achieved with pure chemical compounds that form single crys-

tals. Many of nature's remarkable materials contain mixtures of molecules or microstructures in which inorganic crystals or glasses coexist with organic molecules. Examples include bone, cartilage, shells, leaves, and skin. Here, we address the concept of molecular manipulation of microstructures in inorganic materials, a biologically inspired synthetic tool for the era of

The authors are in the Department of Materials Science and Engineering, Department of Chemistry, Beckman Institute for Advanced Science and Technology, Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.

\*To whom correspondence should be addressed.

materials by design. As discussed here, molecular manipulation of materials implies the use of organic molecules, even in very small amounts, to control the microstructures of inorganic solids. This article focuses on materials in which organic molecules are the minority component; examples of these systems can be found in nature, but the potential exists to discover synthetic analogs of technological interest. The inverse systems (which are predominantly organic) or those with comparable amounts of both types are certainly interesting but resemble more the conventional polymer composites that have been investigated over the past few decades.

Three groups of materials have been selected to illustrate the microstructural concept of molecular manipulation—biomaterials, ceramics, and semiconductors. Biomaterials are defined here as either naturally occurring materials in living organisms or materials designed to repair humans. As discussed below, organic molecules impart toughness to otherwise brittle mineral structures in many organisms (1), and thus synthetic minerals that use molecular manipulators could be excellent candidates for bone replacement in humans. However, there is no reason to limit the role of organic molecules in such systems to toughening functions. Organic molecules could also be used to synthesize highly functional minerals, for example, implants that would carry critical therapeutic agents or molecules such as growth factors that would be useful in tissue engineering.

The ceramic group generally encompasses chemically resistant materials that are designed to withstand elevated temperatures but are usually brittle in nature. Thus, a minority component of organic material in ceramics could also play a toughening role in brittle microstructures but could reduce the high thermal resistance of these materials. If extremely high temperature use is not required, organic manipulators could add a great deal of functionality to ceramic materials. Of course, organics have been used over the past two decades as the precursors of ceramics in the so-called chemical routes to ceramics (such as sol-gel syntheses) (2, 3). Such chemical routes to ceramics have offered a great deal of synthetic and processing flexibility in this group of materials. A different role for organics in ceramic microstructures would be as manipulators of morphology, leaving an imprint of their original presence even after their disappearance at high temperatures (4–6).

In the field of semiconductors, microstructural manipulation with organics is a field that is just emerging but has enormous potential. One could envision organics serving a templating role to access a specific

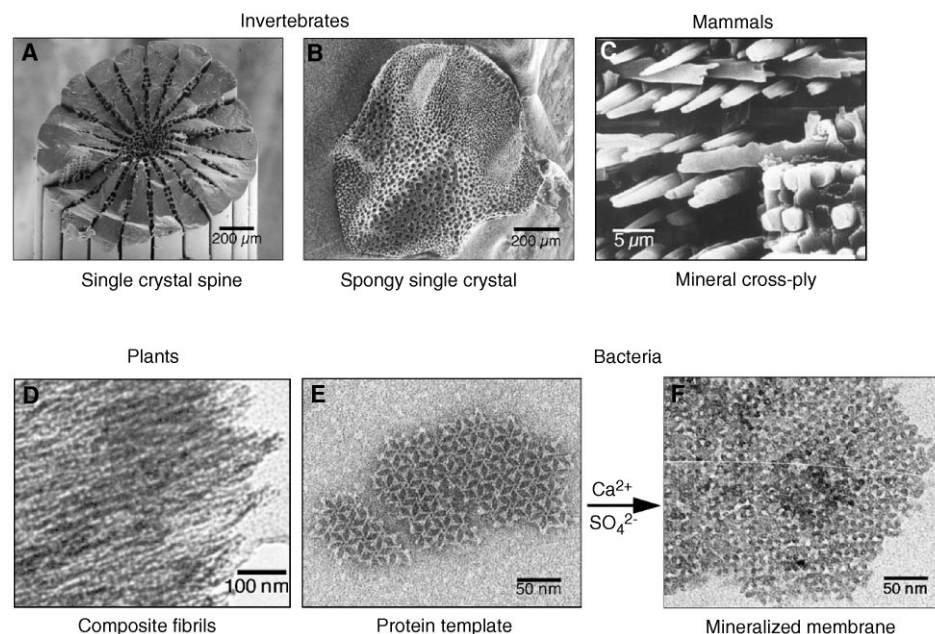
morphology in inorganic semiconductors (7), or one could disperse organic molecules with an electronic or photonic function in semiconducting microstructures. Organic molecules could also help organize semiconducting nanocrystals into functional macroscopic structures (8). We explore here examples in these three areas, which involve work performed in various laboratories, including our own.

## Biomaterials

Among mineralized biological materials, one finds magnificent examples of microstructures in which only a small content of organic matter plays a key role in the determination of properties. Weiner and Addadi (1) have recently reviewed this field and described many examples of these remarkable materials synthesized at ambient temperatures and pressures by various taxonomic groups. Nature's mineralizers use small amounts of organic macromolecules to manipulate nucleation, growth, microstructure, and, consequently, the properties of their mineral-based materials. One example in mammals is the microstructure of tooth enamel in the incisor of a rat. The microstructure, shown in Fig. 1C, contains rods composed of hundreds of spaghetti-

shaped crystals of carbonated apatite. This microstructure resembles the cross-ply configuration of some advanced composites formulated with carbon fibers in polymer matrices. Two other fascinating examples, which are also shown in Fig. 1, are the spongy ventral plate of a starfish, varying in texture at different sites (Fig. 1B), and the sea urchin spine (Fig. 1A), both of which are composed entirely of a single crystal of calcite. The sea urchin single crystal may contain as little as 0.02 weight % glycoprotein, but this small content of organic matter remarkably enhances the mineral's resistance to fracture (9, 10). According to Weiner and Addadi (1), the manner in which the mineral phase and the organic material are organized is one of the key factors contributing to the distinctive mechanical properties in these biomaterials. They suggest that this could be part of the organism's strategy to create more isotropic properties from inherently anisotropic components such as one-dimensional macromolecules and crystalline minerals. This is in fact a very important goal in the design and engineering of composite materials.

The minerals and macromolecules used by nature vary greatly, as do the structural motifs in which these hybrid materials are organized. The macromolecules used by na-



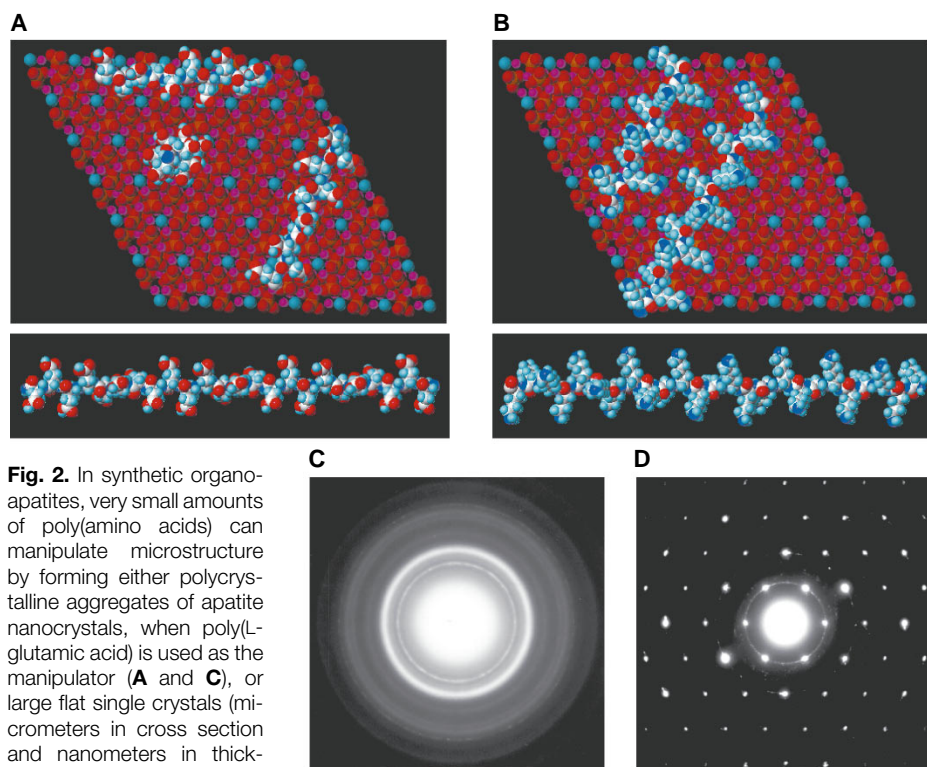
**Fig. 1.** Electron micrographs of molecularly manipulated inorganic microstructures observed in nature. Two unusual calcite single crystals are observed in invertebrates: one is a spine with radial texture in the sea urchin (A) and the other is a sponge with different size pores in the arm of the star *Ophiocoma wendtii* (B) (1) (reproduced by permission of the Royal Society of Chemistry). An example from mammals is observed in the incisor of a rat, which generates crossed elongated crystals of carbonated apatite reminiscent of an advanced composite microstructure (C) (1) (reproduced by permission of the Royal Society of Chemistry). In certain plants, macromolecules can stabilize amorphous silica with a specific morphology (D) [reproduced from (13) with kind permission from Elsevier Science Ltd, the Boulevard, Langford Lane, Kidlington OX5 1GB, UK], and in the membrane of some bacteria, they form highly symmetric templates for mineralization (E and F) [reproduced with permission from (17)].

ture in small quantities to manipulate microstructure include proteins, glycoproteins, and polysaccharides (1). The macromolecules tend to have common structural features, such as a high content of carboxylate groups (such as glutamic and aspartic acid residues in proteins), which lead to interactions between organic chains and mineral precursor ions and also help to attach the macromolecules to solid surfaces. With regard to minerals, two important ones found in endoskeletons and exoskeletons are calcium carbonate polymorphs and calcium phosphates such as carbonated crystalline apatite. An interesting example of microstructural manipulation may be found in the nucleation of either the aragonitic or calcitic polymorphs of calcium carbonate, which differ significantly in mechanical properties (11). In biological systems, macromolecules could also serve to control crystal growth and thus the object's shape by adsorbing to specific crystal planes. The entrapment of these macromolecules in the mineral-based microstructure could then increase toughness in an otherwise brittle material. A possible toughening mechanism would involve their deviation of cracks and absorption of energy from the propagating crack (12). A remarkable example is the toughness of the sea urchin spine shown in Fig. 1A. Other examples of molecular manipulation in biominerals could be related

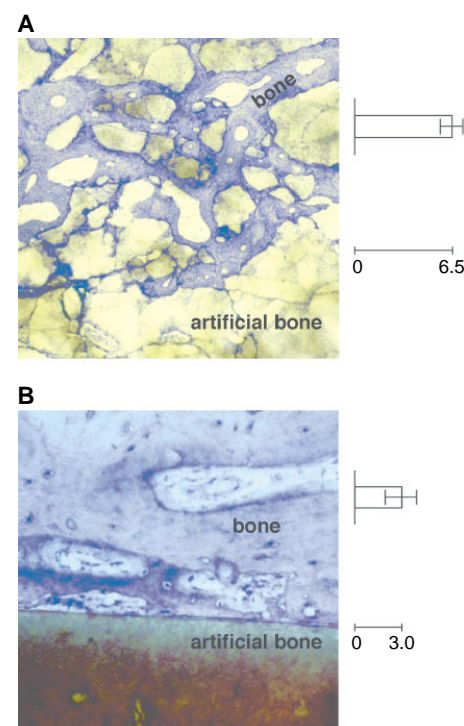
to the stabilization of amorphous minerals [for example, silica (13), calcium carbonate (14), and calcium phosphate (15, 16)] and the formation of microstructures in which there is long-range ordering of mineral particles (13). Biogenic amorphous silica found in branches, leaves, and hairs of certain plants may have microstructures with fibrous, sheetlike, or globular morphology, and it is intimately associated with macromolecular components such as proteins and carbohydrates (13). A micrograph of amorphous silica fibrils found in plants is shown in Fig. 1D. Another interesting system in the present context is the mineralization observed on the cell membranes of some bacteria that can be equal to or exceed their cellular weight (17, 18). In some bacteria, the cell membrane contains a regular arrangement of proteins on its outer surface (S layer) that serves as a template for mineralization (Fig. 1E). In these systems, the resulting mineral nanostructure has the same symmetry and dimensions as the S layer of proteins (see the example in Fig. 1F).

Our laboratory explored nature's use of macromolecules as manipulators of mineral microstructure to synthesize materials designed to serve as human artificial bone (19–21). We have termed these biomaterials “organoapatites,” which are synthesized by the nucleation and growth of hydroxy-

apatite mineral in aqueous solutions of organic macromolecules, including homopolymer poly(amino acids), low molar mass peptides, and synthetic polyelectrolytes. The microstructure of these materials is envisioned as apatite lattices threaded or surrounded by very small amounts of molecularly dispersed organics amounting to only 2 to 3% of the total weight. These small amounts of organic content manipulate dramatically their microstructure and physical properties and in this regard bear some resemblance to the previously discussed calcium carbonates that are modified by occluded proteins. Furthermore, in the case of organoapatites, the chemical structure of the minority organic component can also control the observed biological response when these materials are implanted in bone (21). As illustrated in Fig. 2, B and D, when organoapatites are synthesized in dilute aqueous solutions of poly(L-lysine), one obtains two-dimensional single crystals (micrometers in cross section and nanometers in thickness), whereas small nanocrystals grow in the presence of similar solutions containing poly(L-glutamic acid) (Fig. 2, A



**Fig. 2.** In synthetic organoapatites, very small amounts of poly(amino acids) can manipulate microstructure by forming either polycrystalline aggregates of apatite nanocrystals, when poly(L-glutamic acid) is used as the manipulator (A and C), or large flat single crystals (micrometers in cross section and nanometers in thickness), when poly(L-lysine) is present in the mother liquor (B and D). Note the coherence between the apatite crystal lattice and the amino groups of the poly(L-lysine) chain in (B).



**Fig. 3.** The brittleness of an apatite-based artificial bone material is revealed by the common fragmentation of cylindrical objects implanted in bone (A), whereas mechanically toughened implants can be synthesized by manipulation of the mineral's growth and particle sintering with only 2 to 3 weight % organic macromolecules (B) [see (20, 21) for synthetic details and definition of the fragmentation index, which is given on the right-hand side of (A) and (B)].



and C) (22). We believe that this is explained by the ability of poly(L-lysine) to favor the growth of the ab planes of the crystal. Glutamic acid residues, however, are possibly very effective at nucleating crystals. An illustration of the manipulation of physical properties is shown in Fig. 3, which reveals microscopic evidence of the highly brittle behavior of materials obtained in the absence of organic content and the toughened material formed by poly-ionic organoapatites. Whereas we cannot access for synthetic systems the capabilities of living cells in biogenic microstructures, it is likely that we may discover fascinating tools for microstructural control in cell-seeded forms of these materials in the emerging biomaterials approach known as tissue engineering (23, 24). In this approach, biodegradable synthetic materials acting as scaffolds are seeded with cells to induce the regeneration of natural tissues.

An exciting future prospect in the context of organoapatite biomaterials and other molecularly manipulated inorganics is the use of the organic content to create highly functional minerals. We recently generated an example by synthesizing an organoapatite containing a molecule designed by us

that contains three structural motifs varying in function: the anti-inflammatory drug indomethacin; the amino acid tyrosine, which is potentially adhesive toward solid surfaces; and the precursor monomer to the biocompatible polymer poly(2-hydroxyethyl methacrylate) (25, 26). One could envision future examples of designed functional minerals containing organic molecules, which may include ceramic materials to be used at low temperatures and even semiconductors, in which the organic component contributes an electronic or photonic function in the inorganic lattice.

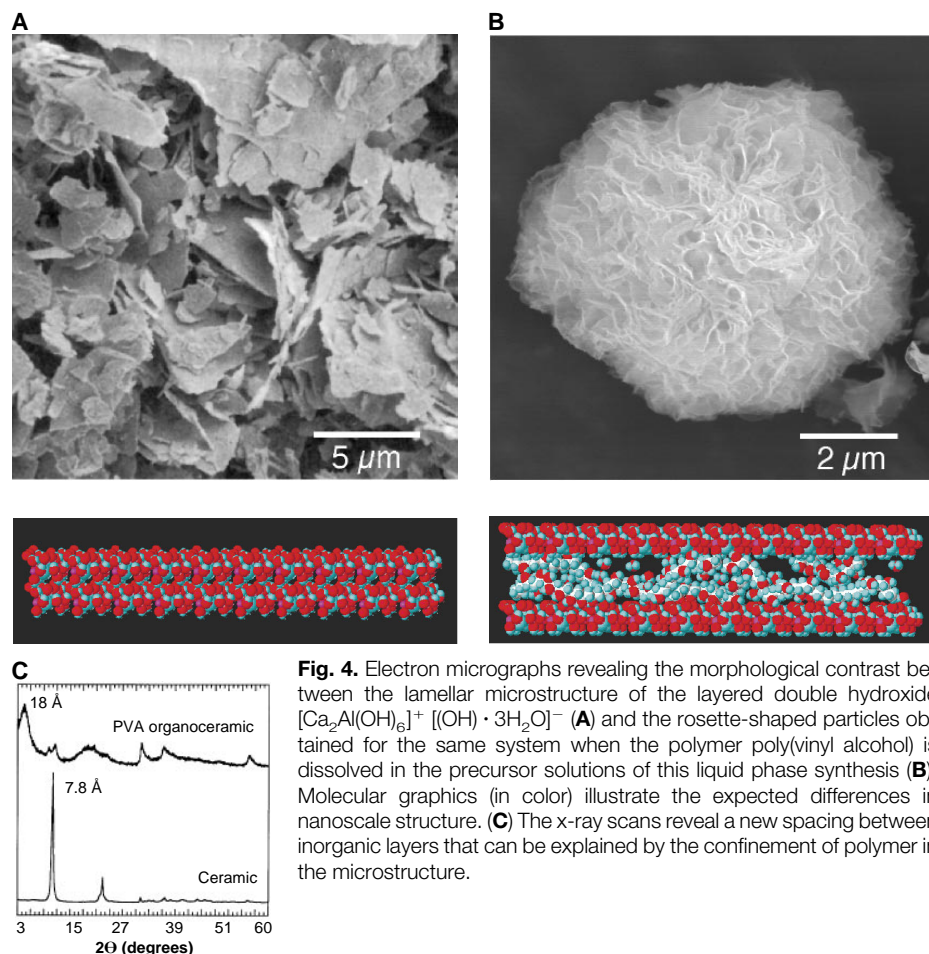
## Ceramics

Many of the metal-nonmetal structures known as ceramic materials have traditionally been synthesized by fusion or sintering of complex mixtures of inorganic compounds such as metal oxides (27). Over the past few decades, new possibilities for their synthesis have been identified by the use of chemical routes, including the sol-gel methods for glasses and ceramics (2). In these methods, the synthesis of the inorganic networks begins at low temperatures with condensation polymerization of multifunc-

tional metal alkoxide monomers and ends with calcination aimed at the removal of the organic by-products of polymerization, solvents, residual monomer, and other organics. There is no question that these methods offer the possibility of more chemically homogeneous ceramics, new forms of fluid precursors, and particle shape control, which is important in further processing. Other approaches in which designed inorganic clusters are synthesized as building blocks for a self-assembling approach to ceramics may eventually emerge as important methods. The concept considered here, however, is the possibility of using organic molecules to drastically change the microstructure of the inorganic lattice of a ceramic material. Some examples are described below.

An interesting recent discovery about molecular manipulation in ceramic microstructures is their sol-gel synthesis mediated by organic surfactants, which leads to mesoporous materials (4, 28–32). The mesoporous microstructure obtained by this method reflects the order parameter of mesophases formed by the self-organization of organic and inorganic components during synthesis. Over the past few years, many mesoporous ceramics have been synthesized, including aluminosilicate (4), titanium silicate (33), zinc phosphate (30), and manganese oxide (34), achieving control of chemical composition, microstructure, and gross morphology (35). These materials can be grown as particles (4), free-standing films (36), films on a variety of substrates (32), and complex morphologies (37). A wide range of chemistries has been used for the inorganic precursors and the surfactants, but many use silica precursors such as tetramethylammonium silicate or colloidal silica (or both) and a cationic surfactant (38). Presumably, the mesoporous microstructure emerges as supramolecular assemblies form that contain the cationic surfactant and the growing metal oxide molecules. It is believed that the nanoscale and microscale symmetry and dimensions of the inorganic phase are controlled by molecular packing constraints and growth rates of the inorganic phase. This method results in structures controlled mostly by kinetics and not thermodynamics (37). Periodic arrays of designer pores imprinted by the surfactant in important materials such as silica may lead to important functional ceramics. These functional ceramics may include interesting catalytic functions and environmental waste remediation properties chemically engineered into the mesoporous microstructure (33, 34, 39).

Self-assembled monolayers (SAMs) (40) provide the opportunity to molecularly manipulate the microstructure of inorganic



**Fig. 4.** Electron micrographs revealing the morphological contrast between the lamellar microstructure of the layered double hydroxide  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+ [(\text{OH}) \cdot 3\text{H}_2\text{O}]^-$  (A) and the rosette-shaped particles obtained for the same system when the polymer poly(vinyl alcohol) is dissolved in the precursor solutions of this liquid phase synthesis (B). Molecular graphics (in color) illustrate the expected differences in nanoscale structure. (C) The x-ray scans reveal a new spacing between inorganic layers that can be explained by the confinement of polymer in the microstructure.

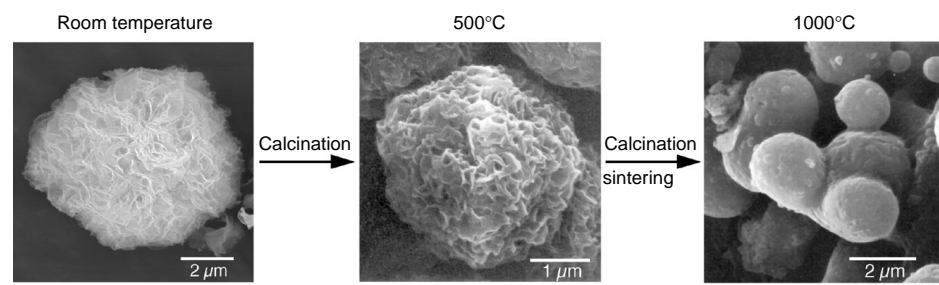
materials when they are used as growth substrates (41). Selection of specific molecules to create the SAM can yield surfaces designed to interact with specific mineral phases, such as sulfonated SAMs for the growth of FeOOH. Through careful control

of solution chemistry and supersaturation, mineral phase growth with specific crystallographic orientation can be induced to precipitate on almost any substrate on which SAMs can be deposited. By patterning the SAM on which the mineral phase

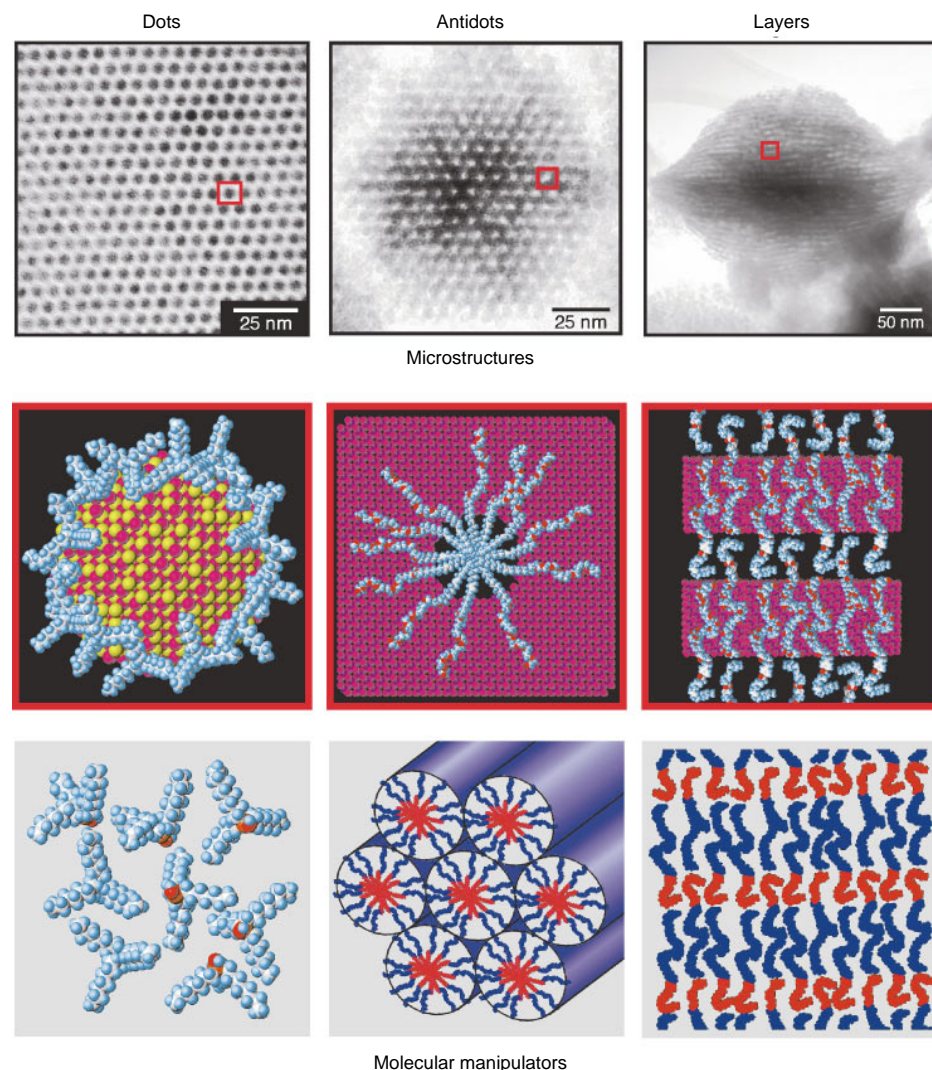
will grow, it is even possible to write inorganic microdomains (42). We describe below another concept in which organic macromolecules modify inorganic microstructures and form composite materials.

A different concept that has been explored in our laboratory is the precipitation from solution of calcium and aluminum layered double hydroxides, such as  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+ [(\text{OH})\cdot 3\text{H}_2\text{O}]^-$ , in the presence of organic polymers. This procedure generates organoceramics in which the organic macromolecules significantly change the morphology and properties (5, 6, 43). Micrographs of the flake-like morphology obtained in the absence of organics and the very different rosette-shaped composite particles obtained in the presence of poly(vinyl alcohol) macromolecules are shown in Fig. 4, A and B, respectively. The organic-inorganic composite rosettes are fairly monodisperse in size, and these ruffled-surface particles have an Al/Ca ratio that is essentially identical to that of the fully inorganic material and an organic content of ~20 weight %. The mechanical properties of bulk materials pressed at room temperature are significantly improved in the organoceramic composition (44).

We believe that the molecular manipulation of microstructure occurs here through the role of polymer chains in nucleation of the inorganic layers. Furthermore, we believe that the polymer becomes intercalated between the inorganic principal planes to produce expanded interlayer spacings. These expanded spacings revealed in x-ray diffraction (XRD) scans (see Fig. 4C) cannot be induced by simple diffusion of the same macromolecules within the nanometer-scale spaces in a stage after precipitation. This barrier presumably arises through the large entropic barriers involved in macromolecular diffusion into such tight spaces. Becze and Xu have argued that this intercalation does not take place and that the polymer is merely involved in nucleation (45); however, we found that the degree of intercalation was highly dependent on the synthetic scheme used (44). On the basis of XRD studies, we found that the molecularly manipulated microstructure can expand and contract reversibly with exposure to moisture, suggesting possibilities for sensing minerals (44). Interestingly, an imprint of the spheroidal composite rosettes remained in the microstructure after organic molecules had vanished and the material had been converted to CaO and calcium aluminate ceramics by heating to 1000°C (6). The rosette skeleton was clearly visible when the structure was almost entirely inorganic at 500°C. These transformations are illustrated by micrographs shown in Fig. 5.



**Fig. 5.** The morphology of inorganic-organic composite particles is preserved as the system is calcined to form a mostly inorganic material (500°C), and the particle's spheroidal contour is still observed as the organic content vanishes and the material transforms to ceramic by 1000°C.



**Fig. 6.** Transmission electron micrographs of three molecularly manipulated microstructures of II-VI semiconductors: a colloidal crystal of CdSe nanocrystals covered by organic surfactants, a colloid of  $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$  punctured by a regular array of cavities templated by cylindrical molecular assemblies of surfactant molecules, and a lamellar particle with alternating CdS and organic layers templated by an organic lamellar mesophase. Below the micrographs, models and schematic representations of the hybrid structures and their respective molecular manipulators are shown in color.



## Semiconductors

Given the well-known materials functionality that is possible with solids of intermediate conductivity between metals and insulators, it would be interesting to develop the field of molecular manipulation of semiconducting microstructures. Over the past few years, some systems have emerged that have begun to explore this area. One example is the synthesis of II-VI semiconductor nanocrystals, which are highly regular in size and shape, by the use of organic surfactants to control the process (8, 46–50). The surfactant molecules coat the nanocrystals, which in turn can self-organize into highly ordered microstructures analogous to colloidal crystals (8). These crystals of nanostructures have potential as large arrays of quantum dots with interesting electronic properties.

Bawendi and co-workers have achieved a very high degree of control over the size of semiconductor quantum dots, generating organically coated CdSe nanocrystallites that are monodisperse within the limit of atomic roughness and soluble in common organic solvents (47). Because the semiconductor crystallites are all virtually the same size, the dots can assemble into faceted crystals of micrometer dimensions or as a closely packed layer on an appropriate substrate (8). Molecular monolayers around the nanocrystals prevent the formation of disordered structures, and self-organization of the quantum dots occurs in a controlled fashion as the solubilizing power of the solvent is decreased. This yields the superlattice of quantum dots shown in Fig. 6. Along with the formation of these two- and three-dimensional networks, semiconductor quantum dots can also be joined with specific chemical linkers, forming, for example, dimers of CdSe with defined interparticle spacings (50). Langmuir monolayers were first used to manipulate the growth of inorganic and organic crystals (51) and more recently as templates for semiconductor growth, resulting in crystallites shaped as rods, triangles, and even a continuous network (48). The driving force for the formation of the observed structures is molecular recognition between monolayer head groups and specific crystallographic faces of the incipient semiconductor crystallite (52).

Our laboratory has studied a different type of molecular manipulation in II-VI semiconductors that achieves the inverse of the quantum dot arrays, namely, a polycrystalline semiconducting continuum with periodic nanometer-sized cavities templated directly by assemblies of organic molecules. We initially reported (7) on the synthesis of colloid-sized particles of

CdS that were punctured periodically by cylindrical cavities 2 to 3 nm in diameter and spaced 8 nm apart in a hexagonal array. Recently, we observed improved fidelity between the template and periodic nanometer-sized cavities by adjusting the reaction conditions (53). We achieved the molecular manipulation of the semiconducting microstructure by doping a hexagonal liquid crystal with precursor  $\text{Cd}^{2+}$  ions and then allowing precipitation to occur by diffusion of  $\text{H}_2\text{S}$  through the highly ordered metal-doped gel. We achieved direct templating by the gel, which was seen because the semiconducting medium copied exactly the characteristic symmetry and dimensions of the lyotropic liquid crystal. We observed an excellent example of this templating effect in a ternary system of  $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ . As shown in Fig. 6, hexagonal symmetry of the liquid crystal is expressed not only in the symmetry and dimension of periodic nanocavities interrupting the semiconducting lattice but also in the shape of the particle itself (54). The microstructure is generated because semiconductor growth is excluded from the nonpolar regions of the liquid crystal, that is, the cylindrical regions in which hydrophobic segments are confined.

Molecularly templated cavities in a semiconducting continuum are interesting features of the microstructure because they could serve many functions. Their presence could produce a periodic array of antidots that could modify electronic properties of the semiconductor (55–57). Alternatively, the cavities could be used to selectively adsorb or transport molecules and also to chemically transform molecules diffusing through the cavities by taking advantage of electronic or photonic properties of the semiconductor. Interestingly, depending on the chemical nature of semiconductor precursors, it is possible to anchor irreversibly the templating molecules in the semiconducting lattice (58). This concept, illustrated in Fig. 6, suggests that molecules with interesting electronic or photonic characteristics could serve as templates but once anchored in the inorganic medium could modify electronic properties such as electron-hole recombination rates. This would represent an electronic analogy to the mechanical function served by occluded proteins in biologically occurring crystals of calcium carbonate.

Inorganic-organic interactions in semiconductor synthesis could open up new avenues to novel microstructures and control of properties. For example, semiconductor-metal transitions (59, 60), as well as absorption and luminescence spectra (46, 49, 61, 62), are molecularly modifiable. To date,

virtually all research on the design of semiconductor devices has involved high-temperature and high-vacuum syntheses followed by patterning with conventional lithographic techniques. However, control of dimensions in the 1- to 5-nm range, as well as novel properties, may emerge with the use of molecular engineering of organics. Our own recent work on mushroom-shaped organic nanostructures could be adapted to template the synthesis of huge arrays of quantum dots with interesting molecular connectors between them (63). Liquid crystals have potential for three-dimensional control in templated syntheses of inorganics, but many challenges still need to be faced to achieve this goal. The potential is based on the possibility of thermodynamic control of dimensions, symmetry, and internal structure through changes in mesogen chemical structure. We illustrate, for example, in Fig. 6 an additional system studied in our laboratory, a lamellar one based on a liquid crystal formed by oligovinyl alcohol amphiphiles and water (64) generating alternating layers of inorganic semiconductor and organic material.

## Conclusions

The examples described in this article involving biomaterials, ceramics, and semiconductors are all based on the use of relatively simple organic molecules to manipulate microstructure. A rather extensive territory could still be explored if one considers the possible use of molecules with controlled stereochemistry, block design, and backbone architecture. The potential outcome could be a toolbox of inorganic materials synthesized directly into specific macroscopic or microscopic shapes, mechanically versatile inorganic materials with combinations of properties not yet offered by conventional composites, and a new set of functions that integrate the properties of both components. It is certainly true that an era of designed hybrid materials of the type discussed here has not yet touched technology and it is not at the present time a totally established chapter in materials science.

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# Pathways to Macroscale Order in Nanostructured Block Copolymers

Zhong-Ren Chen, Julia A. Kornfield,\* Steven D. Smith, Jeffrey T. Grothaus, Michael M. Satkowski

Polymeric materials undergo dramatic changes in orientational order in response to dynamic processes, such as flow. Their rich cascade of dynamics presents opportunities to create and combine distinct alignments of polymeric nanostructures through processing. In situ rheo-optical measurements complemented by ex situ x-ray scattering reveal the physics of three different trajectories to macroscopic alignment of lamellar diblock copolymers during oscillatory shearing. At the highest frequencies, symmetry arguments explain the transient development of a bimodal texture en route to the alignment of layers parallel to the planes of shear. At lower frequencies, larger-scale relaxations introduce rearrangements out of the deformation plane that permit the formation of lamellae perpendicular to the shear plane. These explain the change in the character of the pathway to parallel alignment and the emergence of perpendicular alignment as the frequency decreases.

Self-assembly of block copolymers (1–7), surfactants (8–11), colloidal suspensions (8, 12), and proteins (13) provides a versatile means to create nanostructures with potential applications in biomaterials, optics, and microelectronics. These materials form ordered structures on scales from a few to hundreds of nanometers. Monodisperse, charged colloidal suspensions can assemble three-dimensional lattices (8). Surfactant

systems form a variety of morphologies and can be used as precursors to prepare nanostructured solid materials (10). Similarly, block copolymers (BCPs) assemble a fascinating array of nanostructures. BCPs have the desirable feature that their morphology can be systematically controlled by varying the number of blocks, their lengths, and their chemical compositions. For example, diblock copolymers can form cubic arrays of spheres, hexagonal arrays of cylinders, bicontinuous cubic phases, or lamellae, depending on the relative block lengths (1). Triblock copolymers composed of three distinct blocks (ABC) can assemble even more complex structures (14), such as helical strands surrounding cylinders embedded

Z.-R. Chen and J. A. Kornfield, California Institute of Technology, Chemical Engineering 210–41, Pasadena, CA 91125, USA.  
S. D. Smith, J. T. Grothaus, M. M. Satkowski, Procter and Gamble, Miami Valley Laboratories, Cincinnati, OH 45239, USA.

\*To whom correspondence should be addressed.



## Molecular Manipulation of Microstructures: Biomaterials, Ceramics, and Semiconductors

Samuel I. Stupp and Paul V. Braun

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