

# New Nanofabrication Strategies: Inspired by Biomineralization

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## Abstract

Nature produces a wide variety of exquisite mineralized tissues, fulfilling diverse functions. Organisms exercise a level of molecular control over the detailed nano- and microstructure of the biomaterials that is unparalleled in today's technology. Our understanding of the underlying design principles of biomaterials provides ample opportunities for developing new approaches to materials fabrication at the nanometer and micrometer scale. It is clear that valuable materials lessons can be taught by any organism. I will exemplify this point by describing new nano- and microfabrication strategies and devices that have been inspired by the studies of biomineralization in echinoderms. The topics will include self-assembly, control of crystallization, synthesis of adaptive optical structures, hybrid materials, and novel actuation systems at the nanoscale level.

## Introduction

I was nominated for this award by the Biomechanics Symposium with the expectation that I would probably talk about biologically formed nanostructured glass and the lessons we can learn from these organisms. It would have been a wonderful topic indeed. Just take a look at an amazing creature—a deep-sea sponge (Figure 1).<sup>1-6</sup> The skeleton of the sponge is entirely made of glass, with an array of optical fibers, whose performance and properties are very similar to synthetic optical fibers. They are even made out of the same material—glass. Further, the architecture of the skeleton of this deep-sea sponge is genetically controlled, from the nanometer scale to the macroscale. Starting with the woven hairs of glass that make the inch-wide cage of the entire organism, one can follow the beautiful and sophisticated/structural design, which includes hierarchically assembled plywood structures, laminated glass, and fiber-reinforced glass cement, through the millimeter scale, the micron scale, down to the nanometer scale. In fact, one can teach a course in mechanics and fiber optics entirely based on the design of the glass

produced by the deep-sea sponge. It is also a great lesson in bioinspired architecture, as you can think about this structure as an illuminated mansion built to be inhabited. Indeed, a couple of shrimp live inside this perfectly designed illuminated glass house, which is strong enough to withstand the impact of stones.

Is this a unique example of biological inspiration for materials science? Absolutely not! It does not matter which organism we choose; each of them can teach us valuable lessons in nanotechnology, materials design, materials fabrication, and materials synthesis. It is often surprising to discover the “high-tech” properties of materials produced by nature.

To exemplify this point, I decided to focus on organisms positioned a little higher on the evolutionary scale: echinoderms. Echinoderms are invertebrate marine animals usually characterized by a five-fold symmetry that possess an internal skeleton of calcite plates and a complex vascular system. Figure 2 shows two different echinoderms: sea urchins and starfish. My choice of echinoderms for this talk is due to the fact that various aspects of

nanotechnology can be derived and learned from this system. I will show some interesting lessons in crystal growth,<sup>7-30</sup> dynamic nano- and microstructured optics,<sup>31-37</sup> actuation at the nanometer scale,<sup>38-40</sup> and fascinating examples of self-assembly.<sup>41,42</sup> I will also demonstrate how to improve materials design and device fabrication based on the study of echinoderms.

## Lessons in Nanofabrication of Crystalline Materials

The common theme in my research is the understanding of biomineralization strategies. Nature uses minerals for a wide variety of functions, the most basic of which is the skeletal design and mechanical protection.<sup>43-45</sup> In the case of echinoderms, entire skeletons are built out of calcite crystals. Calcium carbonate, in the form of calcite, in geological specimens or in crystals that are grown in the laboratory are “normal,” somewhat boring, crystals; they always grow as perfectly faceted {104} rhombohedra. Easy cleavage along these facets brings about the major problem of calcite as the structural material—its brittleness. The same calcite, however, is used by nature to construct the skeleton of echinoderms, and its shape reveals unusual curved, beautiful forms and nano- and microscale porosity. Each skeletal element of an echinoderm—its test plates and spines—is composed of one single crystal of calcite. If we examine a



Figure 1. Details of the Western Pacific hexactinellid sponge, *Euplectella aspergillum*, and its skeleton. Photograph shows the underlying siliceous cylindrical skeletal lattice exposed by removal of the organic material. The entire skeleton is made of glass, and the organism is illuminated by the fiber-optical glass crown.

sea urchin spine and a non-biogenic calcite crystal using a routine x-ray, the results are indistinguishable. Nature knows how to grow a patterned crystal in a bottom-up fashion, introduce micro- and nano-porosity without tedious top-down nanolithography, and maintain the single crystalline character of these significantly reinforced inorganic materials.

Can we take this wonderful crystalline material produced by echinoderms and use it as inspiration? We only know a little about this system, but even a simple lesson from echinoderms provides a powerful synthetic strategy. We now understand that biology generally controls the growth of minerals using so-called stereochemical recognition at the organic/inorganic interface. For a materials scientist, this means that inorganic crystals in biological environments usually are templated by specialized macromolecules; in the case of calcite, these were shown to be highly acidic (i.e., richly sulfonated or phosphorylated and rich in aspartic and glutamic acid).<sup>7-10</sup> We can extract these macromolecules from biological systems and try to use them to control crystal formation in the laboratory,<sup>7-12</sup> but it is preferable to take the approach of a materials scientist, using a biomimetic synthetic system that is better understood and easier synthesized. So, instead of using biological macromolecules, we can simply reformulate the idea in terms of the application of a synthetic organic layer that will direct the formation of an inorganic material. For example, using self-assembled monolayers of alkanethiols supported on metal films, we can do a wide range of things: we can functionalize these monolayers with groups that have biological relevance (e.g., we can take acidic groups used by nature for the formation of calcium carbonate crystals), and we can then study the influence of different metallic supports and different symmetries of substrates as templates for crystal growth.<sup>13-17</sup> Our results show that almost every combination of a self-assembled monolayer and a metal support gives extremely uniform



Figure 2. Examples of echinoderms: sea urchins (top) and sea stars (bottom).

orientational control of calcite growth (Figure 3).<sup>14,22,25</sup> The clustering of the data is really impressive; all the crystals in each system grow in an oriented manner and nucleate from the same crystallographic plane, but these orientations are unique and characteristic for different systems.

Our results show that the orientation of crystals is not controlled by epitaxy but largely by stereochemical recognition. We note that the orientation of functional groups in the monolayer is the same as the orientation of anions in the growing inorganic crystal. In other words, the functional groups of the monolayer can be considered surrogate oxyanions for the nucleating crystal that control the oriented binding of the inorganic ions and determines the crystallographic orientation of the nascent inorganic crystals.<sup>14,22,29</sup> Epitaxy contributes to the production of anisotropic strain at the organic/inorganic interface, and this anisotropic strain controls or contributes to controlling the shape—not the orientation—of crystals that grow at these interfaces.<sup>27</sup> This result shows that even small changes in orientation of the functional group can introduce changes in the orientation of growing inorganic crystals. This gives us a good idea for materials design in terms of finely tuning the direction of crystal growth. It may also give us some understanding of the biological processes, in particular, how nature produces such a huge variety of

oriented crystalline materials, with each species showing a characteristic orientation. Our results suggest that, conceptually, it is not necessary to have a different protein to induce differently oriented crystals; small conformational changes in the orientation of functional groups that induce nucleation will give the same result and the ensuing biological diversity.

We can go further, beyond controlling the orientation of crystals, by using another mechanism evolved by echinoderms to produce calcite crystals. The simplest way to describe this approach is to utilize the notion that in biology, there is control of the micro- and nano-environment of crystal nucleation and growth.<sup>8,17</sup> Biogenic crystals do not grow in an open space or on completely uniform bulk organic surfaces. Figure 4 shows the biologically formed calcite crystal and synthetic crystals epitaxially grown on top of the biological substrate. Note that even though the whole substrate is a calcite crystal, new crystals only grow in certain locations. This tells us that certain areas in the biological system are more active for nucleation, and that crystals are selectively induced to form at these locations. In this way, nature creates the sophisticated structures made of elaborate crystalline materials that are nicely patterned on micro- and nanometer scales.

To try to mimic this idea, we used a soft lithography technique introduced by George Whitesides that allows patterning of

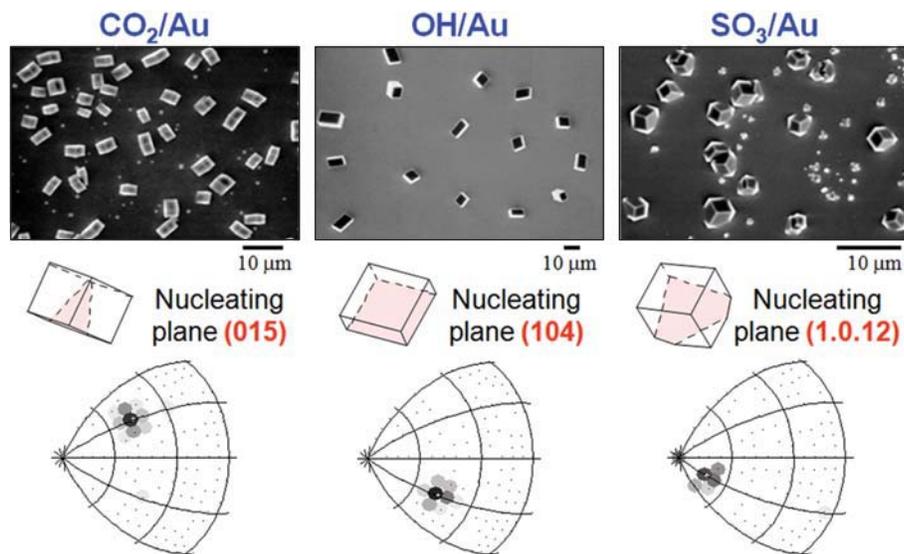


Figure 3. Oriented growth of calcite on self-assembled monolayers (SAMs) supported on gold films. Top: Scanning electron micrographs showing the face-selective nucleation of calcite crystals mediated by the CO<sub>2</sub>-terminated SAM (left); OH-terminated SAM (center); and SO<sub>3</sub>-terminated SAM (right). Middle: computer-generated simulations of the regular calcite rhombohedra viewed down perpendicular to the corresponding average nucleating face (shaded). Bottom: Morphological analysis of the oriented crystals, showing highly uniform, specific nucleation.

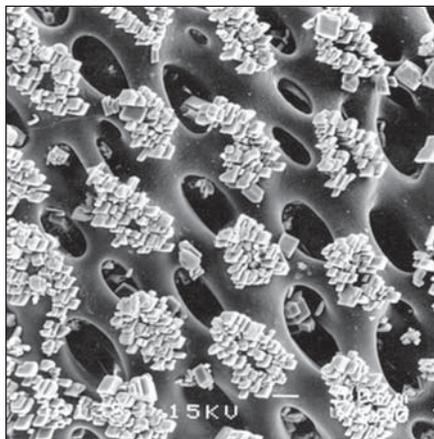


Figure 4. Control of the micro- and nano-environment of crystals nucleation in biological environments. Epitaxial overgrowth of synthetic calcite crystals on the surface of the brittle star spine shows that the nucleation of the newly formed calcite crystals occurred locally at specific “activated” sites.

self-assembled monolayers by microcontact printing (Figure 5).<sup>46</sup> We can now pattern organic nucleation sites in a very ordered manner on the surface and functionalize the rest of the surface with another molecule and use such substrates for crystal growth, thus encouraging the formation of crystals in preferred locations only. Using this approach, nearly every property of crystal growth can be controlled at the micron and nanometer scale.<sup>13–17,23</sup> Highly ordered arrays of uniform crystals can be grown such that all crystals are oriented and nucleated from the same crystallographic plane. We also can control the density of nucleation and crystal size. In our work, we have produced ordered arrays containing precisely one crystal per site (Figure 5a), 100 crystals per square millimeter, or 10,000 crystals per square millimeter; the crystal density is under our control. We also can control the shapes of these crystals by interface engineering combined with the addition of certain additives to a solution that would selectively modulate the crystal growth in certain directions (Figure 5b).<sup>20,24,27</sup> Materials other than calcite, whether organic or inorganic, also can be grown.<sup>26,29</sup> The same approach can be used to control colloidal assembly.<sup>18,19</sup> In other words, we can grow arrays of uniform crystals with precisely defined orientation, density of nucleation, crystallization pattern, and size and shape of the constituent crystallites.

Can we try to do something more complex and grow large *single* calcite crystals patterned on the nanometer and micrometer scale? Of course, we do not want to use top-down manufacturing to drill

holes, etch, and polish crystals to achieve the desired porosity. We want to apply a biological approach, using a bottom-up fabrication strategy, in which the crystals would grow directly into their final sophisticated, porous shapes.

There is yet another lesson in crystal design to be learned from echinoderms that can help us solve this problem. During my PhD work at the Weizmann Institute, we showed that sea urchin larval skeletal elements—spicules (sharp, needle-like structures)—first form an amorphous calcium carbonate structure with a controlled nucleation site that induces the crystallization of the predeposited amorphous material.<sup>10,11,47</sup> Amorphous material has a wonderful feature: it can be molded into any shape, and there are no facets to worry about. It has been shown that mature spines of sea urchins and other marine organisms also use the same approach.<sup>48–50</sup> So, to construct these extremely fancy single-crystalline shapes, one can consider first molding the amorphous precursor phase, then controlling the nucleation site, such that it may propagate through the amorphous phase, which was predetermined in its form, and thus produce one single crystal of any arbitrary shape. Once again, we can use the biomimetic approach by placing just one nucleation site on the surface, with an atomic force microscopy tip, for example. We functionalize the rest of the surface with a self-assembled monolayer, which induces formation of amorphous material, by using our knowledge of biological molecules that are involved in the stabilization of amorphous calcium carbonate in nature, and then we impose any 3D structure on top of it. The first material that forms is amorphous, then nucleation takes place in the predetermined nucleation site, and the crystal propagates through this arbitrary 3D micro- or nanostructure and forms a large, single porous crystal.<sup>21,28</sup>

This new approach to nanofabrication of patterned crystals, which uses amorphous-to-crystalline transitions and templates with integrated patterns, shows yet another extremely important materials property: in addition to determining the elaborate shape of the final crystal, the 3D structure acts as a site for release of both stress and impurities, allowing the growth of very large, defect-free, micropatterned single crystals.

### Lessons in Fabrication of Optical Structures

There is an interesting feature of the skeleton of an echinoderm, which we noticed some time ago; not only does the skeleton have a mechanical function, but it can combine it with the optical function.<sup>31</sup> A brittle star, *Ophiocoma wendtii*, changes

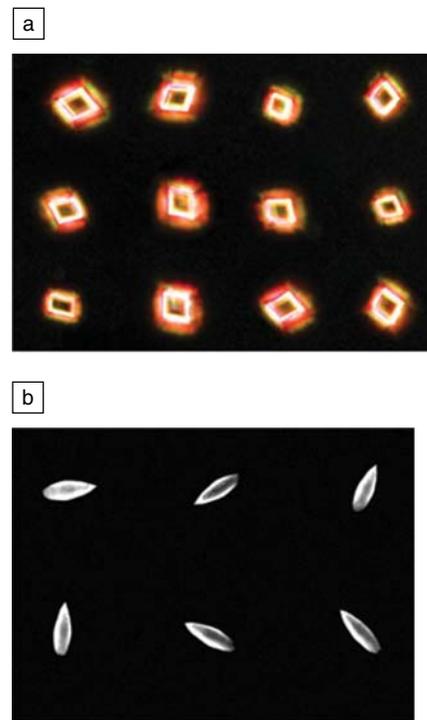


Figure 5. Examples of synthetic bioinspired ordered two-dimensional arrays of single calcite crystals. The densities of nucleation, uniform sizes, and crystallographic orientation are controlled by the micropatterned self-assembled monolayers (SAMs) consisting of regions of  $\text{HS}(\text{CH}_2)_x$  and  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ . (a) Arrays of crystals with the density of nucleation  $N = 100$  crystals/ $\text{mm}^2$  grown selectively from the (104) plane on SAMs of  $\text{HS}(\text{CH}_2)_{22}\text{OH}$  supported on Au(111); (b) arrays of crystals with modified morphology nucleated selectively from the (012) plane on SAMs of  $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$  supported on Ag(111) with the density of nucleation  $N = 10,000$  crystals/ $\text{mm}^2$ . The rice-like shape of the crystals was induced by the addition of Mg ions.<sup>24</sup>

color from black during the day to white during the night (Figure 6a). When we studied the brittle star skeleton, we noticed that the skeletal element that covers the top surface of the arms of the brittle star is coated with extremely well-defined lenses, about 10–40 micron in size (Figure 6b). We raised the question whether these lenses might have an optical function. Calcite is not a very good choice for material for lens construction, because if the lens has any random *hkl* orientation of the constituent calcite, a double-image would form due to the birefringence of this material. Only in the direction of the optical *c*-axis is there single-image formation. In nature, these lenses are oriented in such a way that this requirement is

satisfied: the optical axis is perpendicular to the plate that is covered with these structures. In addition, the lenses are almost perfectly designed—they have no distortions or aberration. These lenses are individually addressed at the receptor cells and are mechanically strong—a great example of

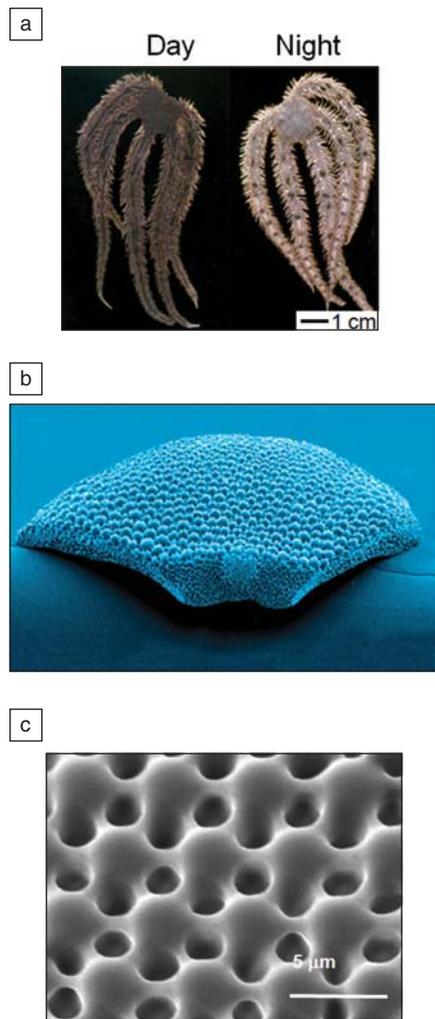


Figure 6. Dynamic optical system in a brittle star *Ophiocoma wendtii*. (a) The same brittle star *O. wendtii*, photographed during the day (left) and during the night (right); color change is due to the movement of pigment that protects the organism from excessive illumination. (b) Scanning electron microscope image of the array of lenses on the surface of the brittle star that are surrounded by the porous network; pigment transport through the porous network leads to the optimization of light transmission through the lenses. The frame of the micrograph is 2 mm across. (c) Synthetic responsive lens array that mimics the dynamic optical system in brittle stars produced by interference lithography.

multifunctionality of biological materials that are optimized for at least two functions, mechanical and optical.<sup>51</sup>

One unusual feature of the brittle star skeleton is that these lenses are surrounded by a porous network, which has a very important role in the biological system. During the day, when there is too much sunlight, these lenses are coated by a pigment that is drawn from within the organism. During the night, when the light is not as intense, this pigment is withdrawn into the structure (Figure 6a). This natural optical system, therefore, is showing its ability to optimize the transmission through the lenses. Right at the focal distance of all these lenses, there is a neural bundle that collects the signal going through the lens. As mentioned previously, the organisms are black during the day and white during the night. In biological literature, it was suggested that this color change is related to mimicry.<sup>51</sup> However, if it were mimicry, one would expect the organism to be white during the day and black during the night. In reality, it is the adaptive movement of pigment through the porous microlens network that gives rise to the organism's color change.

This inspirational finding could aid in the design of biomimetic adaptive optical structures. If we are able to produce lenses, we could couple them with a porous system and combine it with microfluidics. This could be used to fabricate dynamic micro- and nano-lens arrays, which would respond to light intensity in the way it occurs in the organism. We can fabricate similar structures through the amorphous-to-crystalline transition in calcium carbonate by using the approach of crystal engineering described earlier,<sup>21</sup> but we do not have to apply the same materials that are used by nature. We can simply reformulate the construction principles that nature suggests for materials that are better understood or easier to form.

Other approaches are available to generate lenses, such as photoresists reflow, ultraviolet curing of liquid droplets, and self-assembly of beads. In order to combine microlenses and the fluidic network, we decided to use a three-beam interference lithography to create synthetic polymeric (non-calcitic) lenses surrounded by a porous network (Figure 6c).<sup>52</sup> These structures can be used to channel light-sensitive liquids and, in this way, to change transmission in response to the environment and create dynamic optics that would respond to different wavelengths of light. We can place them on curved surfaces to create dynamic arbitrary microarrays of lenses that are similar in design and function to microlenses that

brittle stars have developed as a survival mechanism, just using a different material.

## Lessons in Actuation at the Nanoscale

By examining the skin of the echinoderm, we may be able to learn something about actuation. Echinoderm means "spiny skin." In between the arrays of spines on the surface of echinoderms, there are amazing structures in a shape of microflorets, called pedicellaria, that constantly open and close (Figure 7a). It is believed that they provide an antifouling mechanism through this constant actuation and pattern formation.<sup>51</sup> Echinoderms are, in fact, extremely clean organisms; there is no settlement of microorganisms or dust on their surfaces.

In order to replicate this system on a scale about 100 to 1,000 times smaller, on the nanoscale, we can create nanospines through regular lithography. Figure 7b shows Si nanospines approximately 200 nm wide with a high aspect ratio of about 50. They are static, however, and there

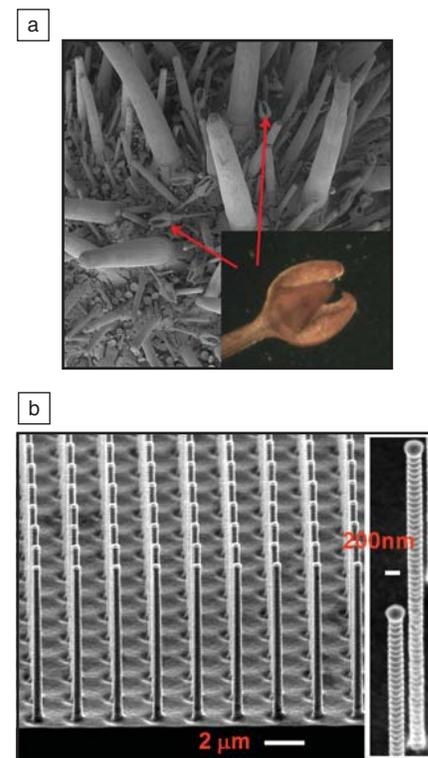


Figure 7. (a) Moving spines and pedicellaria on the surface of a sea urchin; the frame of the micrograph is 5 mm across, while the inset is 100 μm across. (b) Array of synthetic high-aspect-ratio nanospines fabricated in Si that mimic echinoderm skin at the nanometer scale.

is nothing dynamic about them. If we want to reproduce the adaptive nature of echinoderm spines, we will need to add a muscle that will move these Si spines. A hydrogel muscle is a possibility, as hydrogels are responsive—they can shrink or swell in response to environmental cues. When the hydrogel and silicon nanopines are combined, by performing polymerization in confinement, dynamic *actuating* spines are created.<sup>38–40</sup> The polymer, in the dry state, can bend or tilt the nanostructures and return them back to the upright orientation in the extended, swollen state (Figure 8a). Figure 8b–8c shows a dry case, in which the spines are lying down, and a wet case, in which they are all standing up. The actuation time is about 60 milliseconds, if we place a droplet of water or apply humidity to the hydrogel. This is the first realization of environmentally responsive reversible actuation at the nanometer scale.

We could control the wetting properties of these nanostructures by starting with a system where the nanostructures are stiff enough so the contraction of the polymer does not produce sufficient force to bend them. In the dry state, this structure is hydrophobic, while in the wet state, when hydrogel covers the nanostructures, it becomes hydrophilic. For smart materials, smart clothes, or smart coatings, we require the opposite transition. The challenge is to make a structure that is hydrophilic when the environment is dry but becomes superhydrophobic when the environment is wet. To achieve this property, the nanopines were embedded in the hydrogel layer without the attachment to the substrate (see Figure 8a). In the dry state, they lie down, and the surface becomes hydrophilic (Figure 8b); in the wet state, they stand up again, and the material is superhydrophobic (Figure 8c).<sup>39</sup> This is a reversible transition; the same material goes back and forth between these two states.

To control the direction of actuation, we can use a patterned confining surface that introduces differences in thickness, thus mapping the stress field into the polymer layer (Figure 9a). By using a confining surface with a particular topographic design, any patterned movement is possible.<sup>38,40</sup> All the structures can be bent in one direction if a striped confining surface is applied (Figure 9b, top). More complex structures could be generated: florets that open and close reversibly made by using honeycomb-bearing confining surfaces (Figure 9b, bottom) or microtraps composed of four nanopines clustered together in a dry state and extended in the wet state in a very similar manner to pedicellaria on echinoderm surfaces (Figure 9c–9d).

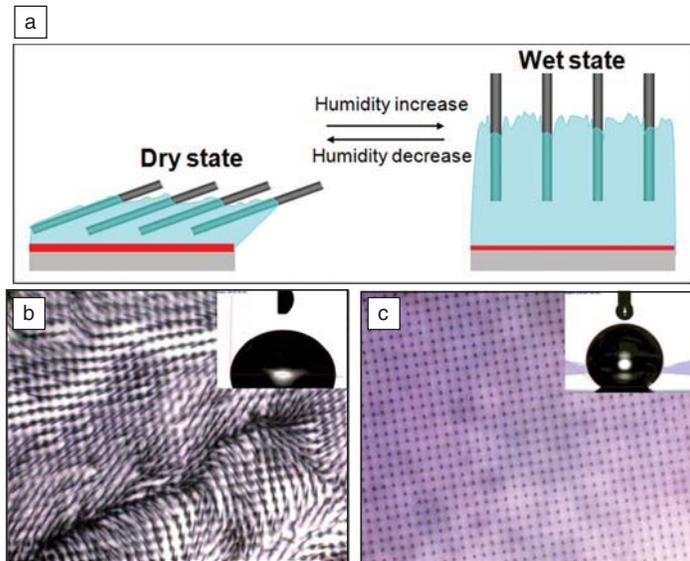


Figure 8. Design of smart actuated surfaces with reversible superhydrophobic-hydrophilic transitions. (a) Schematic illustration of the dynamic rearrangement of the nanopines driven by the hydrogel contraction/swelling in the dry and wet states. (b) Optical micrograph of the surface in the dry state reveals highly tilted spines. The surface is hydrophilic (see inset). (c) Optical micrograph of the surface in the wet state reveals nanopines standing perpendicular to the surface and its hydrophobic character (see inset). The frames of the micrographs in (b) and (c) are both 100  $\mu\text{m}$  across.

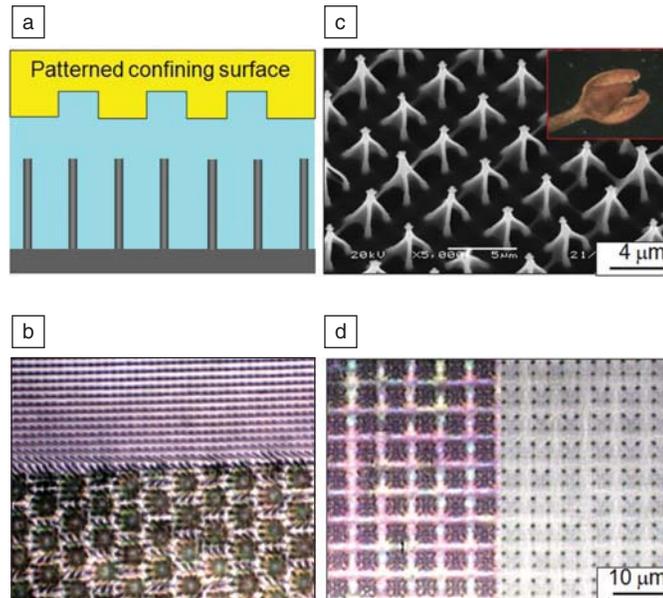


Figure 9. Controlling the patterned actuation of nanopines. (a) Schematic presentation of the synthetic procedure that leads to the coordinated, patterned movement of the spines. The gel is synthesized in the confinement between the nanopines and a topographically patterned substrate that determines the direction of actuation. (b) Uniform orientation of the tilted nanocolumns is templated by the patterned confining surface that is bearing lines (top); regular array of microflorets is templated by the substrate bearing a honeycomb pattern (bottom). Each “flower” in (b) is 30  $\mu\text{m}$  in diameter. (c) An example of a complex pattern, showing an array of microtraps, in which every group of four attached nanocolumns is held together by the hydrogel. (d) Optical micrographs imaging microtraps shown in (c) in a dry (left) and a wet (right) state. The switching of the nanocolumns from bent fourfold clusters to a vertical orientation is clear. This reversible movement resembles the structure and actuation of pedicellaria (see inset in c).

In fabricating such nanospines, we have introduced a cheap, fast, double-replication technique in which we start with a silicon master (Figure 10) and produce a negative replica of it in an elastomeric material. Using this elastomeric mold, the original geometries can be recreated out of polymers, biomolecules, and ceramics with different mechanical properties.<sup>41</sup> By taking our mold and deforming it (squeezing, stretching, twisting, or shearing), we were able to produce various nanostructures that have completely different geometries from the original silicon substrate. In particular, we can create geometries that are not easily made by lithographic techniques (e.g., tilted or twisted nanospines).<sup>41</sup>

### Lessons in Dynamic, Hierarchical Self-Assembly

If we make the nanostructures out of responsive polymeric materials or from material that is doped with nanoparticles that respond to a magnetic field, an electrical field, or other external stimuli, we can move and assemble these structures without the hydrogel.<sup>41</sup> Depending on the mechanical properties of the polymeric bristle and geometry of the structure, we have obtained unexpected results and discovered dynamic hierarchical helical self-assembly at the nanoscale that occurs upon drying in the bristle immersed in a liquid (Figure 11).<sup>42</sup> In regime I, if the bristles are sufficiently stiff, the meniscus may bend them slightly, but when the liquid dries, they spring back to an upright orientation, and no assembly occurs. If the length is larger than the critical length, these nanostructures can bend sufficiently to touch each other, so we can create arrays of nicely clustered tetramers of the bristle (regime IIa).

If the surfaces are adhesive enough, the clusters try to increase their contact through chiral rearrangement of the nanospines, which is energetically more favorable for these structures (regime IIb). If they are even more flexible, then such chiral rearrangement would finally result in twisting of these pillars to produce helical assemblies (regime IIc).

We can make the structures softer and more adhesive. In regime III, each of these clustered tetramers act as one bristle and continue to assemble into the higher-order helical units composed of  $4 \times 4$  clusters. By carefully controlling the mechanical and adhesive properties of these structures, we can go to the next level, regime IV, in which units of 16 interact through meniscus-driven evaporation and create very large self-assembled domains. These large assemblies all have the same unique

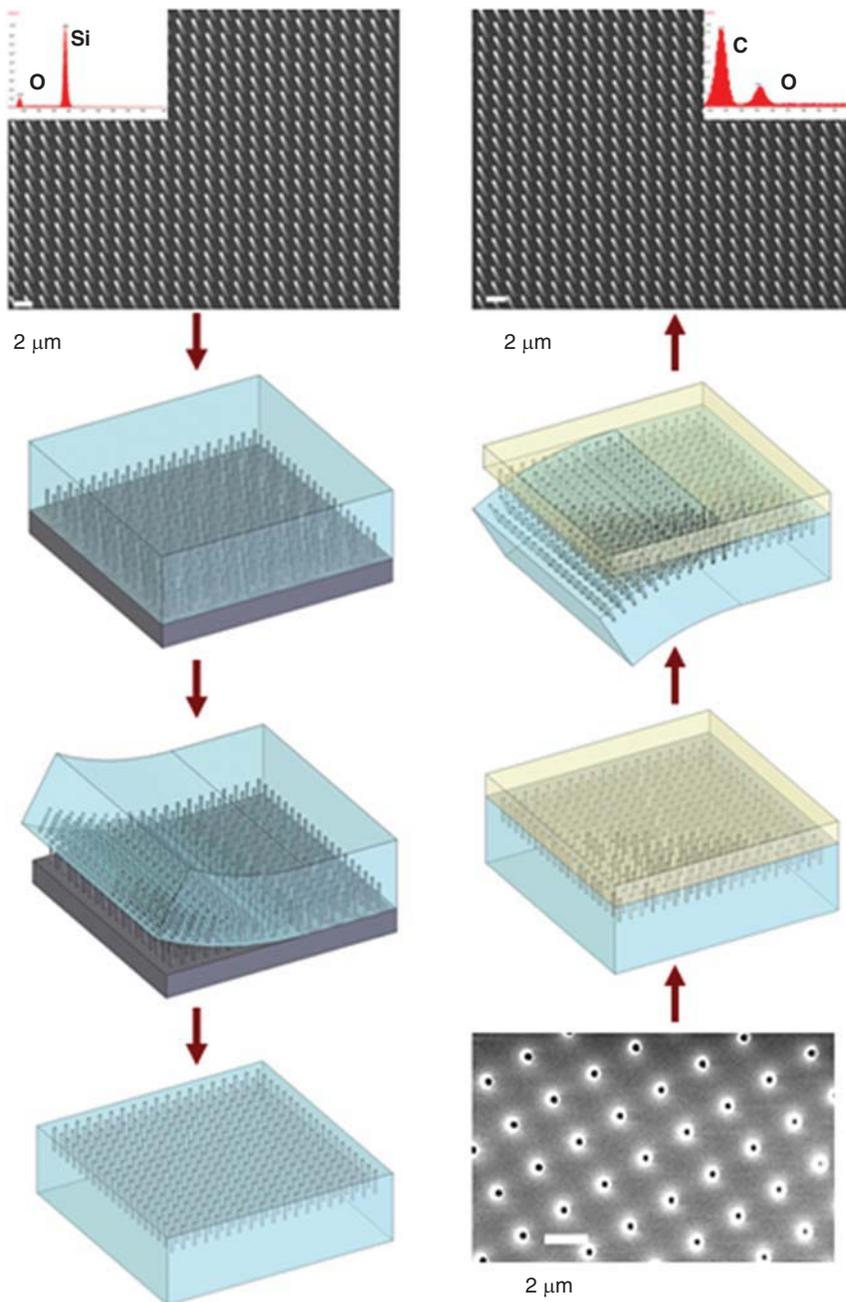


Figure 10. Two-step soft-lithography process for creating replicas of nanostructured surfaces with high-aspect-ratio features in a variety of materials. From top left down: Scanning electron microscopy (SEM) image of an exemplary original nanostructured surface—a silicon master bearing a square array of nanospines. The inset is an EDS (energy dispersive) spectrum. Next, the PDMS (polydimethylsiloxane) precursor is poured onto the master, treated with an anti-sticking agent, and cured. The cured PDMS is peeled off from the master. The negative PDMS mold, which contains an array of high-aspect-ratio wells corresponding to the posts of the positive master, is surface-treated with an anti-sticking agent. From bottom right up: SEM image of the PDMS mold, revealing the high-aspect-ratio wells. Next, the liquid precursor (polymer, liquid metal) is poured onto the negative PDMS mold and cured. The PDMS mold is peeled from the cured positive replica, and a SEM image of an exemplary nanostructured replica is fabricated from epoxy resin. The inset is an EDS spectrum. The replicated structure is geometrically indistinguishable from the master on the left.

feature: they are chirally arranged and twisted and allow for the production of whirlpools of nanostructures. The system can be stopped at any hierarchical level by changing the properties—the liquid or geometry, mechanics, and adhesive properties of the nanostructures.

The helical clusters produced by this approach are racemic in nature. How can we control handedness in our system? We can induce uniform chirality using a couple of methods. For example, we can tilt the nanostructures using the mold shearing in such a way that they form a small angle with the crystallographic direction in the underlying uniform lattice (Figure 11b, top). When these nanostructures assemble with one another, they can only approach each other from the same side. In this way, twisted dimers, tetramers, or higher order assemblies can be created that have highly uniform handedness (Figure 11b).<sup>42</sup>

Such evaporation-induced assembly produces surprisingly regular, nearly crystalline, arrays of clusters. The basis for the generation of this exceptional order is the following: when the first cluster forms (induced by a local defect in the nanobristle or by the local changes in evaporation), it generates asymmetry of the meniscus at the position of its immediate neighbors, which means that the force on the next post would be asymmetric, and it would move in the direction away from the first cluster and assemble with the next post. The process would propagate through the entire bristle, so naturally this approach will generate highly ordered large-area arrays of assembled nanostructures.<sup>42</sup>

These unique twisted clusters can be used in a variety of ways. For example, since there is a pronounced entanglement and chirality in these structures, they can grab and hold cargo. Figure 12 shows the cluster formation in the presence of spheres, and the spheres are securely trapped inside during the chiral assembly of the nanostructures and held by the nanofingers. This is a new way of capturing and releasing nano- and microspheres within the assembling bristle.

**Conclusions**

Using one inspirational system, the echinoderms, one can come up with a set of new approaches to the synthesis of ordered, oriented crystalline materials at the nanoscale. The same organism also inspires the design of tunable nano- and microlens structures. We can create novel, hybrid hydrogel-actuated nanospines and nanotraps similar to echinoderm skin. We also can consider how to generate unusual

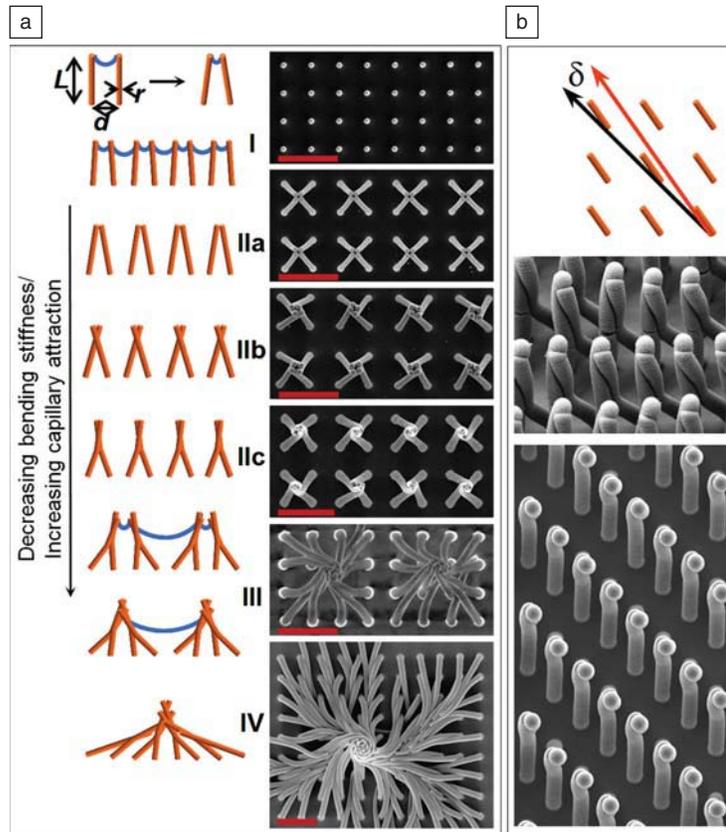


Figure 11. Chiral self-assembly of polymeric bristle. (a) Schematic diagrams (left) and corresponding scanning electron microscopy (SEM) images (right) showing the morphogenesis of helical patterns, from the first-order unclustered nanobristle to the fourth-order coiled bundle, until halted by the elastic field that penalizes large deformation (see text for detailed explanation). Scale bars are 4  $\mu\text{m}$ .  $L$  is length of a bristle,  $r$  is the radius of a single bristle, and  $d$  is the distance between two neighboring bristles. (b) Controlling the handedness of the assembling clusters by using an array of nanocolumns that are slightly tilted in the direction that forms a small angle  $\delta$  with the underlying array. SEM images show uniform chirality of the assembled dimers. The frames of the micrographs in (b) are both 10  $\mu\text{m}$  wide.

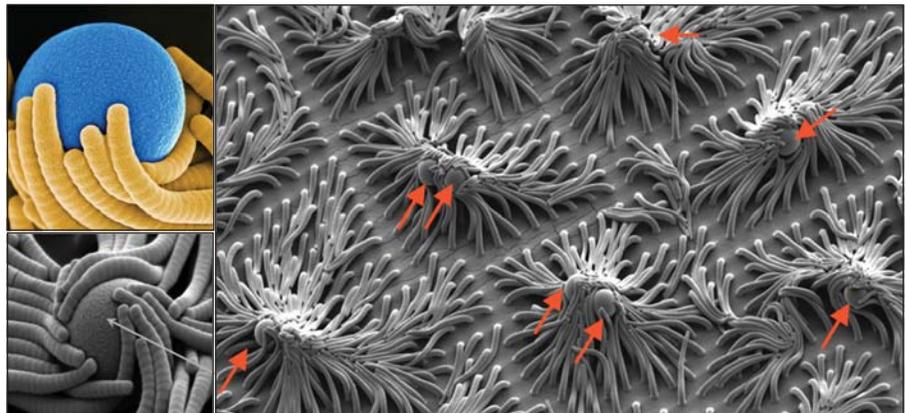


Figure 12. Illustration of the adhesive and particle trapping potential of the helically assembling bristle. Scanning electron microscopy images show the capture of the 2.5- $\mu\text{m}$  polystyrene spheres (indicated by arrows). Right image is 50  $\mu\text{m}$  wide. Left two images show magnified views depicting a single sphere trapped through the conformal wrapping of the nanobristles. The top-left image is 3  $\mu\text{m}$  wide, and the bottom-left is 5  $\mu\text{m}$  wide.

self-assembly into hierarchical patterns and impose chirality on the assembly. These bioinspired structures have the potential for use in a variety of fields: actuators for controlled release, artificial muscles, tunable optics, highly ordered crystalline materials for photonics and biomedical applications, and surfaces with controlled wettability. Obviously, echinoderms provide new, bioinspired concepts in materials chemistry, nanotechnology, and engineering.

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