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## Silicon and Sun

In his lab facing the Pacific Ocean, Daniel Morse is learning new ways to build complex semiconductor devices for cheaper, more efficient solar cells. He has an unlikely teacher: sea sponges.

By Kevin Bullis



Daniel Morse holds a species of marine sponge commonly known as Venus's flower basket. (Credit: Gregg Segal)

In his beachfront office overlooking the Santa Barbara channel, Daniel Morse carefully unwraps one of his prized specimens. An intricate latticework of gleaming glass fibers, it looks like a piece of abstract art or a detailed architectural model of a skyscraper. But it's actually the skeleton of one of the most primitive multicellular organisms still in existence--a species of marine sponge commonly known as Venus's flower basket. Morse, a molecular biologist at the University of California, Santa Barbara, wants to know how such a simple creature can assemble such a complicated structure. And then he wants to put that knowledge to work, making exotic structures of his own.

The lowly sponge has come up with a remarkable solution to a problem that has puzzled the world's top chemists and materials scientists for decades: how to get simple inorganic materials, such as silicon, to assemble themselves into complex nano- and microstructures. Currently, making a microscale device--say, a transistor for a microchip--means physically carving it out of a slab of silicon; it is an expensive and demanding process. But nature has much simpler ways to make equally complex microstructures using nothing but chemistry--mixing together compounds in just the right combination. The sponge's method is particularly elegant. Sitting on the seabed thousands of meters below the surface of the western Pacific, the sponge extracts silicic acid from the surrounding seawater. It converts the acid into silicon dioxide--silica--which, in a remarkable feat of biological engineering, it then assembles into a precise, three-dimensional structure that is reproduced in exact detail by every member of its species.

What makes the sponges' accomplishment so impressive, says Morse, is that

it doesn't require the toxic chemicals and high temperatures necessary for human manufacture of complex inorganic structures. The sponge, he says, can assemble intricate structures far more efficiently than engineers working with the same semiconductor materials.

This primitive creature and a number of other marine organisms have become an inspiration for researchers who hope to find simpler and cheaper ways to build inorganic structures, such as semiconductor devices, for use in computer microchips, advanced materials, and solar cells. The goal is to make silicon and other inorganics self-assemble into working electronics in the same way that the sponge assembles silica into complex shapes (see "[Others in Bio-Inspired Materials](#),"). Energy-intensive, billion-dollar semiconductor fabrication facilities might then be replaced by vats of reacting compounds. But while practical industrial processes are still some way off, scientists are coming to understand how sponges and other sea creatures perform their microengineering miracles.

Morse and his team, for instance, are already using biological tricks learned from the sponge to make new forms of semiconductors with intriguing electronic properties, including the ability to convert light into electricity--properties that could be useful in making cheaper, more efficient solar cells. His group, says Morse, is building "structures that had never been achieved before."

## **Start from Scratch**

The seawater tanks outside Morse's lab are teeming with colorful starfish and corallimorpharians, exotic creatures similar to sea anemones. But Morse and James Weaver, a postdoc in the lab, are more interested in an unremarkable-looking rust-colored blob: an orange puffball sponge, a type of sponge that ordinarily lives in rock crevices just off the Santa Barbara coast. If the Venus's flower basket is the glass cathedral of sponges, this is the straw hut. The shapeless creature appears not to have a skeleton at all; but once the researchers dissolve away the living material of its exterior, a handful of tiny glass needles remain, each only two millimeters long and thinner than a human hair.

Although Morse ultimately wants to understand sponge skeletons that are more complex, these simple needles are a good place to start. Scientists have long known that at the core of the glass needles are strands of proteins, but no one understood what they did or how they related to the needles' construction. So Morse and his colleagues began by isolating the genetic code for one of the proteins--which as a family they came to call "silicateins"--and ran their results through a huge database of known proteins. They weren't expecting a match, but they found one--immediately. The protein was similar to a protease, an enzyme found in the human intestine that is involved in the breakdown and digestion of food.

"It was very bizarre," says Weaver. "Why does the protein that templates the formation of the glassy skeleton of a sponge have anything to do with a protease?" The researchers began to suspect that the silicateins did more than merely serve as a passive template. Indeed, they found that unlike any other enzyme previously studied, a silicatein can do double duty. It actively produces building materials such as silicon oxide--in a sense, by digesting compounds in the seawater--and then causes the materials to line up along its length to form the needle-shaped glass of the sponge skeleton. No such enzyme had been discovered, Morse says, "in all the study of biomineralization, which has gone on for a couple of hundred years."

Morse reasoned that if silicateins were so good at producing silicon oxide, they might also be able to produce the types of metal oxides that make good semiconductors in electronics and in some kinds of solar cells. He was right. "At 16 degrees Celsius, the temperature at which the sponge lives in the cool water right offshore from our lab," Morse says, "this enzyme will catalyze the formation and stabilize the formation of crystal forms of metal-oxide semiconductors that can't be made conventionally except at very high temperatures."

The result suggested a less expensive way to make semiconductors at lower temperatures, but there was a potential problem: contamination. "A biologist is ecstatic when they get a purity of, say, 90 percent. A chemist is ecstatic when they get a purity of 99 percent," says Morley Stone, a biochemist who directs research in biotechnology and materials for the Air Force Research Labs at Wright-Patterson Air Force Base, near Dayton, OH. "But an electronics engineer or someone else who needs to make devices--they want to see materials that have five nines of purity behind them, at least." He adds, "Oftentimes, when you take these biological approaches, you can grow some interesting things and get some interesting morphologies, but they're nowhere close to having the end-state purity that you would need in a final device."

Morse and his colleagues knew that if they hoped to make semiconductor materials for cheap but efficient solar cells, they would probably need a chemical synthesis technique that took its cue from the sponges but avoided the messy biology. The sponge's secret, they discovered, was that amine and hydroxyl chemical groups in the enzyme produce the silicon oxide and assemble it in the required way. That meant that all the chemicals a new synthesis technique would require could be found in ammonia and water. The researchers found that by mixing molecules containing the metal oxides' precursors into water, and then exposing the mixture to ammonia gas, they could create thin films of highly crystalline semiconductors--materials useful for electronics. "This is the breakthrough that gets us into the domain of practical usefulness," Morse says.

Moreover, the crystals have a complex nanostructure that could improve the performance of photovoltaic devices. Near the surface of the water, the

concentration of ammonia gas is relatively strong, so this is where the semiconductor crystal starts to form. As the ammonia slowly diffuses deeper into the water, however, it causes crystals to grow down into the mixture, producing a thin film that is not uniform but rather comprises a network of needles or flat plates each merely a few billionths of a meter thick. That network could be the basis for a more efficient solar cell.

## **Solar Dreams**

The crystalline-silicon solar cells that currently dominate the photovoltaic market are expensive--so expensive that the energy they produce costs several times as much as energy generated by fossil fuels. One reason is the high price of their raw materials. Silicon is extremely abundant on earth, but it doesn't exist as a pure element; instead, it's bound up with oxygen and other elements--in sand, for example. Making pure silicon requires a lot of energy.

To lower the costs of solar cells, researchers have looked for ways to cut down on the amount of silicon they use. Some have turned to less expensive thin films made from cadmium telluride or copper indium diselenide. Extremely thin layers of these new semiconductors can absorb the same amount of light as thicker slabs of crystalline silicon. Morse's fabrication technique could be an inexpensive way to make such thin films; in addition, the nanostructure that his method produces is particularly well suited for absorbing light and converting it into power.

A challenge in designing solar cells is making sure that the electrons dislodged when light hits a semiconductor create a current. When a photon strikes a solar-cell material, the result is both a free electron and its positive counterpart, called a hole. If these can be pulled apart quickly to opposite electrodes, an electrical current results. However, the difficulty of separating them before they recombine and dissipate energy as heat is "one of the major roadblocks for higher-efficiency solar cells," says Aravinda Kini, program manager for biomolecular materials research at the U.S. Department of Energy.

Morse's structures could surmount this roadblock. The network of crystalline projections could be immersed in a transparent solid or liquid electrode. Light would pass through the electrode, where it would be absorbed by the crystal. Because the surface area of the structured thin film is high (in one material, 90 to 100 times that of a traditional thin film), many of the electron-hole pairs generated by the light would be near the electrode interface; as a result, they could quickly separate, with one charge carrier moving into the transparent electrode and the other carrier traveling through the crystal to exit at the opposite electrode.

Already, Morse and colleagues have made more than 30 types of semiconductor thin films and tested their photovoltaic properties. They are

now working to incorporate the semiconductors into functional solar cells. At the same time, Morse continues to develop new biologically inspired methods for assembling materials, with an eye to additional applications, including semiconductor devices for safer, higher-power-density batteries and smaller memory chips; he is also interested in creating laminated fibers for ultrastrong building materials.

But excited though he is by the potential applications of his work, Morse remains at heart a molecular biologist. Even as he talks about how his research could lead to better solar cells, he gazes out the window at the dolphins frolicking in the harbor. And he's still devoted to understanding the mechanism behind the complexity of the sponge. Once again he examines the exquisite skeleton of the Venus's flower basket, though he's no doubt seen it thousands of times. "This was made of glass, by a living creature," he exclaims. "It's incredible!"

*Kevin Bullis is Technology Review's nanotechnology and materials science editor.*

## Others in Bio-Inspired Materials

Researcher	Goal	Strategy
Joanna Aizenberg, Lucent Technologies, Murray Hill, NJ	Strong, self-healing building materials and more-resilient optical fibers	Understanding how sponges assemble inorganic materials
Ilhan Aksay, Princeton University	Self-healing materials and better biosensors	Investigating sea-shells and other biological systems
Angela Belcher, MIT	Better batteries and advanced materials for electronics, energy, and medicine	Engineering viruses to assemble materials
Samuel I. Stupp, Northwestern University	Better sensors and solar cells	Using peptides to direct the formation of inorganic structures