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Learning from biology to create new materials

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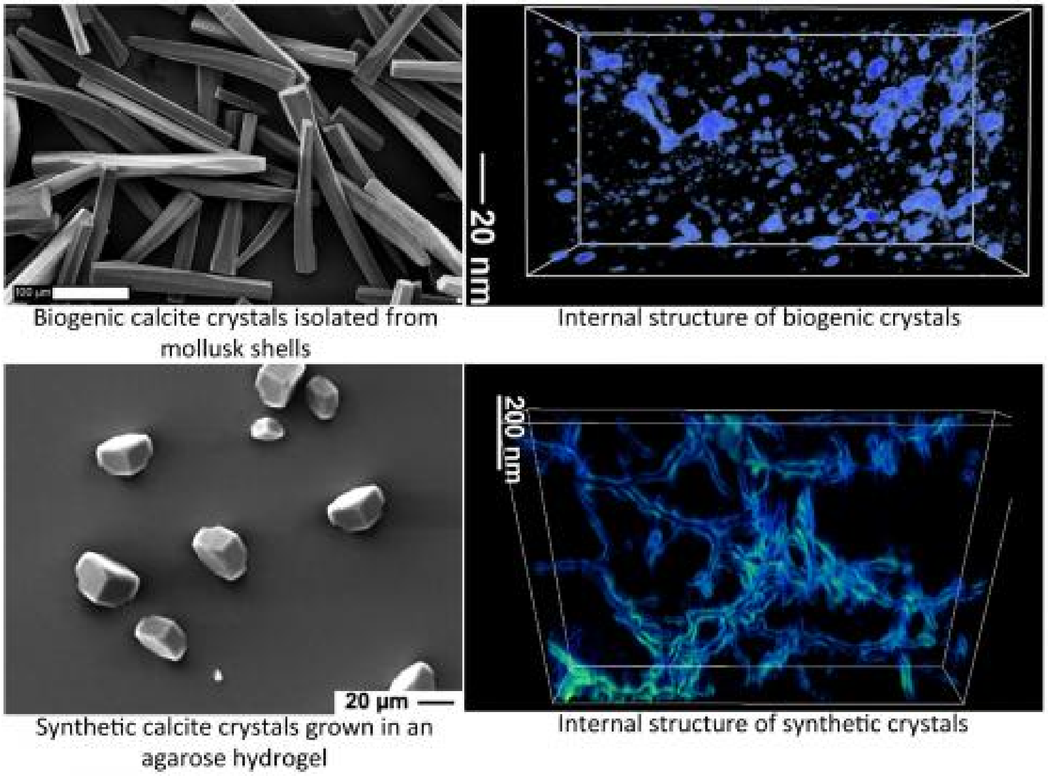

Biogenic calcite crystals isolated from mollusk shells

Internal structure of biogenic crystals

Synthetic calcite crystals grown in an agarose hydrogel

Internal structure of synthetic crystals

Top left: Scanning electron micrograph (SEM) of calcite crystals (also called prisms) isolated from the prismatic layer of Atrina rigida (pen-shell mollusk). **Top right**: 3-D reconstruction of the internal structure of the calcite prisms. The blue areas represent organic-filled voids within the crystal. The technique used to acquire this image is annular dark field scanning transmission electron microscopy (ADF-STEM) tomography. **Bottom left**: SEM of synthetic calcite crystals grown in an agarose hydrogel. **Bottom right**: ADF-STEM tomography showing a 3-D reconstruction of the internal structure of the synethic calcite crystals grown in an agarose hydrogel. The structures outlined in blue represent the agarose fibers that are incorporated into the single crystal of calcite. Credit:

Estroff Lab, Cornell University

In nature, some organisms create their own mineralized body parts—such as bone, teeth and shells—from sources they find readily available in their environment. Certain sea creatures, for example, construct their shells from calcium carbonate crystals they build from ions found in the ocean.

"The organism takes brittle carbonate and turns it into a structural shape that protects it from predators, and from being bashed against the rocks," says Lara Estroff, an associate professor of materials science and engineering at Cornell University. "There is much scientific interest in how the organism controls the crystal growth, and what mechanisms are involved in strengthening and toughening the shells, especially in comparison to their components, which are brittle."

Researchers such as Estroff are very interested in synthesizing this kind of biology in the lab, and creating new organic and inorganic materials that mimic the "biomineralization" that occurs in nature, so they can gain a better understanding of how these natural processes work.

"We are trying to learn the techniques from the organisms, and apply them in the laboratory," says the National Science Foundation (NSF)-funded scientist, a synthetic chemist by training. "Part of it is creating simplified systems so that we can tease apart the more complicated mechanisms that are going on in biology. I am not recreating biology in the lab. I am learning from biology to create new materials."

Estroff's primary research focus is to discover the role of gels in crystal formation. Hydrogels, which are gels made in water, similar to Jell-O, are involved in a number of natural biological systems, including the mother-of-pearl in mollusk shells, tooth enamel in mammals, even otoconia, which are tiny particles found in human ears. These substances are composed of both organic and inorganic materials; often the organic components form a gel. Estroff wants to know their purpose.

"Is there something special about a hydrogel in directing crystal growth?" she asks. "Does it change properties? Is it somehow responsible for giving rise to organic-inorganic composites?"

Understanding and controlling crystal growth is very important in many industrial fields, chief among them the manufacture of pharmaceuticals, since many drugs are in crystalline form, and "it's of vast importance to know how to modulate the solubility of crystals and how they pack into tablets," she says.

There also may be potential applications in producing biomaterials for bone and tooth repair, and in creating more functional inorganic materials, such as substances structured at the nanoscale that could enhance energy storage, for example in batteries. "Being able to manipulate these crystal structures down to the nanoscale opens up a lot of opportunities," she says.

Estroff is conducting her research under an NSF Faculty Early Career Development (CAREER) award, which she received in 2009. The award supports junior faculty who exemplify the role of teacher-scholars through outstanding research, excellent education and the integration of education and research within the context of the mission of their organization. NSF is funding her work with $472,773 over five years.

The project focuses on observations, both in nature and in the laboratory, of macroscopic, single crystals with incorporated polymer fibers and other macromolecules. The project aims to understand the mechanisms by which these polymer networks become incorporated into macroscopic, single crystals.

Her lab, in studying crystal growth mechanisms in gels and their relationship to biomineralization, is trying to answer at least three questions. "First, what is the internal structure of these crystals, and where does the gel material become trapped?" she asks. "Second, can we understand the mechanism of how it is trapped to control how much is trapped? And, third, what effect does this material have on the mechanical properties of the crystals?"

To find the answers, her team developed a synthetic analog to the biological system. Using agarose, a more purified form of the gel agar-agar, they grew their own crystals in the lab, then compared them to crystals grown without gel in an ordinary water-based solution, and later to natural biological crystals.

During the process, they ran a high resolution electron tomography scan of their samples, creating a three-dimensional image of the gel-grown crystal, which "was the first time that people had actually seen how the organic phase can be incorporated in the crystal," she says. "A crystal is an order array of ions, and a polymer is a floppy, poorly-defined blob. How do you accommodate this floppy blob into this ordered array?"

In comparing their synthetic crystals to natural ones, "there were similarities and differences," she says. "We now have the best image of how these objects are incorporated and now can start asking questions about the structure-property relationships, including how this internal structure translates into changes in the mechanical properties. We've been poking at the crystals and looking at the response."

As it turns out, "these organic inclusions mechanically strengthen and toughen the material in both biological crystals and synthetic crystals," she says. "The organic material that is trapped within the crystals makes them stronger and harder—more resistant to fracture—than their geologic counterparts with no organic material."

The researchers' next step is to synthesize other materials. "We'd like to find out if we can grow different types of crystals in different types of gels," she says. "We're now pursuing that route."

As part of the grant's educational component, Estroff teaches a course on biomineralization for both graduate students and undergraduates. "One of my goals is to get them reading primary literature and analyzing it," she says. "They also go out and look for biomineralizing organisms on campus. They go to local streams and bring them back to the lab."

She also is trying to recruit more female students to her department. She is the faculty advisor to a group known as WIMSE, which stands for Women in Materials Science and Engineering, and has organized a mentoring program where freshmen and sophomores are paired with juniors and seniors who, in turn, are paired with graduate students. The enrollment of women in the materials science and engineering major has grown from 10 percent to 30 percent during the last five years.

"Having a group creates a critical mass," she says. "It's really had a positive impact."

Provided by National Science Foundation

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