



## PERSPECTIVES



A layer of iridescent and resilient nacre constitutes the inner layer of mollusk shells.

## BIOINSPIRED MATERIALS

# Growing a synthetic mollusk shell

Three-dimensional organic templates control calcium carbonate precipitation

By **Francois Barthelat**

**T**he deposition of dissolved minerals is usually harmful and can cause the failure of boilers or heat exchangers. Likewise, uncontrolled calcification in our bodies can cause kidney stones or failure of aortic valves. Yet mineralization is also critical in our bones and teeth to achieve stiffness, strength, and hardness. In these materials, biomineralization is

controlled and harnessed through intricate organic templates that guide the growth and shape of crystals (1). As a result, bones, mollusk shells, diatoms, and corals have organic shapes that bear little resemblance to the angular crystals typical of geology. On page 107 of this issue, Mao *et al.* (2) report the biomimetic synthesis of nacre-like material fabricated by controlled mineralization of a multilayered organic template based on chitosan.

Nacre, also called mother-of-pearl, is the iridescent material found in the interior of mollusk shells. It features a “brick-and-mortar” microstructure, in which microscopic tablets of calcium carbonate (about 0.5  $\mu\text{m}$  thick) are bonded by nanometers-thick layers of chitin and proteins.

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Mollusks “grow” nacre through a complex sequence that starts with the secretion of a multilayer organic template (see the figure, top). Calcium carbonate slowly crystallizes at multiple locations simultaneously, filling the template and forming a highly regular, three-dimensional (3D) microscopic brick wall.

The final material is not only stiff and hard because of its high mineral content (>95% by volume) but is also surprisingly tough (it resists crack propagation and impacts). The micromechanisms of deformation and fracture in nacre are distinctive and involve crack deflection along the tablets, crack bridging, and “sliding” of the microscopic tablets over one another over large volumes (see the figure, bottom). These mechanisms make nacre three orders of magnitude tougher (on an energy basis) than the brittle mineral of which it is made, providing superb protection to mollusks (3). This level of toughness amplification has not been achieved to this day with any synthetic composite.

Can we make synthetic materials that duplicate the structure and mechanics of natural nacre? This question has been a focus of research for two decades. Conventional methods do not work well to make nacre-like composite materials (4), so creative approaches such as freeze-casting (5), magnetically assisted slip-casting (6), 3D printing (7), and laser engraving (8) were recently developed. These methods can produce composite materials with a large volume concentration of aligned inclusions at the microscale (5, 6), but “perfect” brick wall-like structures can only be achieved at larger-length scales (7, 8). Controlled mineralization is still of high interest because of the highly controlled structures it would enable at the microscale (9). Hydrogels have been successfully used as templates for mineralization (10) but only up to moderate levels of mineral content, in the form of isolated aggregates. Sequential layer-by-layer mineralization can produce highly mineralized nacre-like materials, but the method is relatively expensive and limited to thin films (11, 12).

The mineralization method proposed by Mao *et al.* is a breakthrough because it successfully combines two critical steps: the fabrication of a large volume of a 3D multilayered template of chitosan with controlled microscopic spacing between the layers, and the complete mineralization of this template up to very high mineral contents (91% volume of calcium carbonate). The material is formed in only a couple of weeks (compared with years for natural nacre). A silk fibroin, infiltrated at the interfaces between the mineral layers, serves as the deformable mortar. The final material duplicates many of the features of nacre, including its brick-and-mortar microstructure and the nanostructure of the individual mineral tablets. In terms of mechanics, the weak interfaces in the material deflect cracks, which results in an increase in toughness (13). This synthetic nacre is about four to five times less “tough” than natural nacre (on an energy basis) but is 100 to 200 times tougher than the pure mineral.

This fabrication method could serve as a “sandbox” with which to study the fundamentals of biomineralization in highly controlled and tunable environments, by using different combinations of minerals and polymers as raw ingredients. This method could also be used to make large volumes of nacre-like bone grafts that would duplicate the mechanical and in vivo response of natural bone, an urgent challenge in orthopedics (14). Because the method works with various sets of organic and inorganic ingredients, it could also lead to many new “bioinspired” engineering materials. In particular, this method could lead to materials that are both very hard and tough, two properties that are mutually exclusive in traditional engineering materials (15). ■

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## A tough act to follow

