

Formation Mechanism of Columnar Nacre Proposed

Nacre, or mother-of-pearl, a composite formed by alternating sheets of organic matrix and platelets of aragonite, exhibits remarkable mechanical properties. To date, its formation mechanism had not been completely elucidated. Recently, however, P. Gilbert from the University of Wisconsin, Madison; M. Abrecht from the Synchrotron Radiation Center, Madison; D. Ariosa from the Swiss Institute of Technology, Lausanne, Switzerland; and their colleagues proposed a growth mechanism for nacre after using x-ray photoelectron emission spectromicroscopy and x-ray absorption near-edge structure (XANES) spectra to obtain information about the orientation of the nacre platelets making up the aragonite layers. Their results were published in the June 29 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.98.268102) and then featured in *Science* (July 13, p.175; DOI: 10.1126/science.317.5835.175d).

X-ray photoelectron emission spectroscopy, a surface-sensitive technique that enables imaging and extraction of spectroscopic information from a single layer of

nacre platelets or from a polished cross section including many layers, provided carbon, oxygen, and calcium maps that, under the appropriate illumination, showed the crystallographic orientation of each nacre platelet with respect to the polarization of the x-rays. The researchers found that, whereas carbon and oxygen showed similar variations, the Ca distributions appeared completely homogeneous. The different intensities observed in those element maps were due to the different angle between the *c*-crystallographic axis for each aragonite platelet and the polarization vector of x-rays. The spectromicroscopy data showed that platelet orientation is conserved across only 1–40 layers in each column. Furthermore, the growth direction of nacre cannot be identified with the *c*-axis of the nacre platelets, as is usually assumed, because the *c*-axis is oriented differently in neighboring columns of platelets.

The researchers proposed a simple formation mechanism considering that the organic matrix sheets are formed first, with preformed randomly distributed nucleation sites. One possibility is that these nucleation sites become active at an appro-

priate stage of the growth process, when a STOP-active organic molecule on side *n* of the organic matrix sheet arrests aragonite growth for platelet *n* along the growth direction, while its counterpart START-active organic molecule on the side *n* + 1 of the same organic matrix sheet is activated and a new aragonite platelet *n* + 1 is nucleated. Another possibility is that the nucleation site is porous and it simply allows crystal *n* to grow through it to start the growth of crystal *n* + 1. The researchers said that “the resulting scenario reconciles apparently discrepant lines of evidence, and encompasses the present results and all other data currently available on the mystery of abalone nacre formation.”

JOAN J. CARVAJAL

Nutrition-Driven Nanoassembly of Gold Colloid on Growing Fungi Results in Microwires

In recent years, structurally diverse forms of microorganisms have been used as templates for the fabrication of inorganic nanostructures. In most cases, attachment of nanoparticles to the micro-organism surface involves sequence-specific recogni-

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tion by biomolecules, facilitated by functionalization of the inorganic nanoparticle surface. For example, monolayers of colloidal gold nanoparticles self-organize on fungal mycelia when the nanoparticles are surface-functionalized with oligonucleotides. However, J. Dutta of the Asian Institute of Technology, Thailand, P. Melin of the Swedish University of Agricultural Sciences, J.G. Hilborn of Uppsala University, Sweden, and their colleagues have developed a more facile route, not requiring nanoparticle surface functionalization, to fabricate gold microstructures 1–3 μm in diameter and lengths exceeding a few millimeters.

As reported in *Advanced Materials* (Vol. 19, p. 77, DOI: 10.1002/adma.200600911), Dutta and co-researchers developed a procedure in which monosodium glutamate reduces chloroauric acid to form colloidal gold nanoparticles, about 15 nm in diameter, stabilized by glutamate. Conidia (i.e., asexual, non-motile spores) from *A. niger*, *A. nidulans*, or *Neurospora crassa* were added to the colloidal gold nanoparticles without any additional nutrients. In a control experiment, the conidia were added to a dilute glutamate solution without gold particles. Although mycelia

were clearly observed under an optical microscope within one week for all cases, those grown in gold colloidal solution, when extracted and dried in air, displayed a bright golden color in reflected light, showing that the gold nanoparticles had agglomerated into a thick coating. The researchers observed that the deep-red colloidal gold solution turned colorless, demonstrating that the gold nanoparticles were depleted from the colloid because they attached to fungal cell walls.

Glutamate acts as a carbon and nitrogen source for bacteria and fungi, which can transaminate glutamic acid to form other amino acids. Therefore, the researchers said, their fabrication technique makes the colloidal solution not just cytocompatible but nutritive for fungal growth. In another control experiment, in which a pregrown fungus was added to the glutamate-stabilized gold colloid, no gold coating was observed on the developed hyphae (i.e., the long, filamentous branching cells), demonstrating to the researchers that only actively growing fungi can assemble colloidal nanoparticles on hyphal walls. The researchers proposed that the region around a growing hypha becomes depleted of glutamate

ions through their consumption, causing a charge destabilization leading to agglomeration of gold nanoparticles onto the hypha within this region.

The gold-coated hypha collapsed during observation with an electron microscope, yielding structures that the researchers deemed appropriate for strip resonators and antennae for radio-frequency circuitry. For these flattened structures, the researchers measured a resistivity close to that of pure gold. Supercritical carbon dioxide extraction served multiple purposes: It caused the inner, water-based materials in the fungus to dry out while the desiccated cell walls stuck to the interior of the tubular nanoassemblies, and it caused the nanoparticles to rearrange so that they did not collapse, resulting in tubular assemblies. The researchers said that post-fabrication treatment could lead to structurally stable free-standing gold microtubes. The researchers said that their process “has the potential to be extended to the self-assembly of charge-stabilized colloidal nanoparticles of a wide range of materials into novel structures, utilizing the symmetry and structural shapes dictated by micro-organisms”.

STEVEN TROHALAKI

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