

Single Crystals with Complex Form via Amorphous Precursors

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amorphous materials · biomineralization ·
crystal growth · morphogenesis · nanostructures

Controlled morphogenesis of solids is of great importance in science and technology, as many properties of solid bodies depend on their size, shape, and organization. Consequently, much research effort is invested to obtain control over precipitation events. One strategy to generate solids with controllable shape is the application of templates, which act as a mold for the subsequent precipitation reaction. This approach works well for amorphous and thus isotropic materials, which can adapt to any shape, replicating even structures down to the range of only a few nanometers. This property is exploited, for example, in the so-called nanocasting approach, which is especially attractive for the generation of porous materials.^[1,2]

Crystalline materials, however, are much more difficult to template since they are anisotropic in nature with vectorially different atomic arrangements dictated by their unit cell, which are periodically replicated in the crystal lattice of the homogeneous body. Single crystals exhibit well-defined faces with defined angles, which is the general understanding of a crystalline substance. The predefined anisotropy of the crystal-building units potentially conflicts with the spatial constraints of an external template with complex shape.

Biominerals, on the other hand, often show very complex morphologies with curvature and without any obvious crystal faces. One example is the skeletal elements of sea urchins. Although they are considered to be single crystals of calcite, the thermodynamically stable CaCO_3 polymorph, they have a very complex shape (Figure 1, left). This complexity is in large contrast to the rhombohedral form which is normally adopted by calcite (Figure 1, right).

Biominerals exhibit complex shape and structure, hierarchical organization, and superior materials properties, and they are synthesized in aqueous environment under ambient conditions, an attractive “sustainable” synthesis strategy. Therefore, biominerals are useful archetypes to learn about nature’s morphogenesis strategies of crystalline substances.

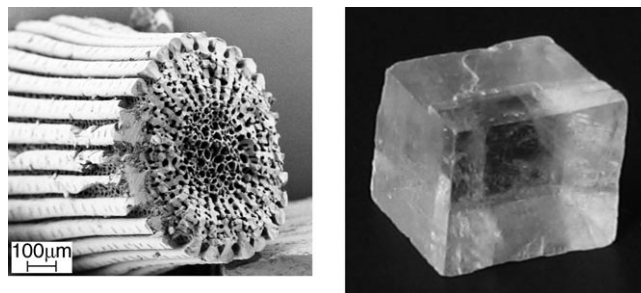


Figure 1. Left: SEM image of a fracture surface of a sea urchin spicule showing the spongy morphology with curvature. Right: Macroscopic geological calcite single crystal.

As biomineralization usually takes place in a spatially confined reaction environment, it is a promising strategy to use a hard template to generate complex crystal morphology. By using a hydrophobic polymer replica of a sea urchin skeletal plate, Meldrum and Park were able to synthesize single-crystal calcite replicas with the complex morphology of the original sea urchin skeleton (Figure 1, left).^[3] However, the synthesized replica single crystals are small (< 1 mm) and are limited by the necessary slow growth of calcite at the applied low ion concentration necessary to achieve only a single nucleation seed. Otherwise, polycrystalline materials result, which do not replicate the template.^[3] Other reported templating strategies create macroporosity in single crystals from latex nanoparticles with subsequent particle removal.^[4–6] Often, the single crystals just exhibit surface porosity;^[4,5] if the latex surface is appropriately modified, an inclusion into the single-crystal interior can also be achieved.^[6] All such macroporous single crystals have a limited size on the order of tens of micrometers.

In nature, much larger templated mineral structures can be found, like the sea urchin spine shown in Figure 1, thus implying that nature can use a different mineralization strategy. In recent years, it has become obvious that some large single-crystal biominerals are not formed from their ion constituents but from amorphous precursor phases, which can form independently of the mineralization event as a material depot.^[7] This process is also well known from polymer-controlled mineralization.^[8,9]

Such a strategy has clear advantages for living organisms since the synthesis of amorphous phases avoids the osmotic stress generated in cells for high ionic strengths, avoids large

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amounts of solution to be transported for the formation of a sparingly soluble crystal, and, most importantly, allows for the adaptation of any complex shape after molding the amorphous phase into a template prior to crystallization.^[10]

For example, the beautiful and complex shape of a sea urchin spine (Figure 1) is formed via an amorphous phase, as revealed by spine regeneration experiments.^[11] In biomimetic mineralization, the application of an amorphous precursor phase has also proved useful for introducing curvature into single crystals, as demonstrated for cylindrical CaCO_3 formed in the small pores of a track-etch membrane, which was completely filled with the amorphous precursor prior to crystallization.^[12] This approach only works up to a certain pore size; with larger pore sizes, polycrystalline calcite is obtained.

Another possibility is the use of liquid precursors, which can be observed for CaCO_3 and some other minerals in systems containing a tiny amount of a polyelectrolyte like poly(acrylic acid) or poly(aspartic acid). These liquid CaCO_3 precursors could be used to fill the nanosized gap zones in collagen fibrils by capillary forces,^[13] to replicate a macroscopic hydrogel template of a sea urchin spine,^[14] or to synthesize macroscopic artificial nacre,^[10] which was found to be indistinguishable in structure from the original biomineral by electron microscopy. However, the samples were polycrystalline,^[14] or the single-crystalline units had only very limited size,^[10] in contrast to the single crystals obtained with the hard hydrophobic polymer templates used by Meldrum et al.^[3,4]

The formation of a single crystal with complex form on the millimeter scale via an amorphous precursor phase could first be achieved by Aizenberg et al. for CaCO_3 in a quasi-two-dimensional morphology on a self-assembled monolayer (SAM) on a micropatterned surface, which induced the formation of an amorphous calcium carbonate (ACC) film.^[15] Nucleation with controlled orientation of the CaCO_3 crystal towards the SAM was achieved by introduction of a defined single nucleation site with an AFM tip. An important finding was that the micropattern not only acts as a template, but also for release of water and impurities, and is involved in the release of mechanical stress generated by volume shrinkage of ACC by crystallization.^[15] Formation of large single crystals requires distances of less than 10–15 μm between template units.^[15] All methods known so far have the disadvantages of either limited size of the micro- and nanopatterned single crystals^[3–6,10,12–14] or a complicated preparation procedure.^[15] These problems can be overcome with the straightforward approach towards nanopatterned CaCO_3 single crystals reported by Li and Qi.^[16] A colloidal crystal of monodisperse polymer latex with carboxyl groups was employed as a template on a filter membrane with subsequent suction of a freshly prepared ACC dispersion through the template. This process led to template infiltration by ACC and replication into a single crystal with nanosized features after subsequent crystallization induced by a single nucleation event (Figure 2), after which the template was removed. The nanosized latex is well below the critical size for template features;^[15] its interface can thus serve for release of water, impurity, and stress.

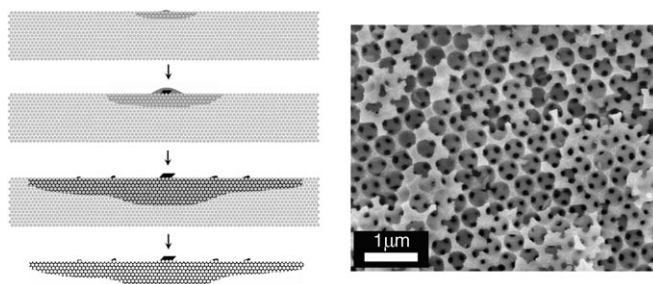


Figure 2. Left: Schematic illustration of the formation process of flat nanopatterned calcite single crystals.^[16] Right: SEM image of a calcite single crystal templated by a colloidal crystal of 450-nm latex particles showing the hcp order of the initial colloidal crystal template.

In the center of the surface of the templated calcite single crystals, oriented with the (104) surface parallel to the surface of the former colloidal crystal, a rhombohedral seed crystal is always found (Figure 2, left), which indicates a single nucleation point. The calcite single crystals exhibit dendritic shapes owing to their growth at the expense of ACC under non-equilibrium conditions and still exhibit a size on the micrometer scale. Larger crystals should be possible by fine-tuning of the crystallization conditions since the ACC precursors can supply enough material for the growth of large single crystals. Delicate control is required for the complete template infiltration by ACC as well as for the subsequent crystallization owing to the balance between maintaining a single nucleation event for the production of a large oriented single crystal and the necessary supply of enough material for growth. If crystallization can be tuned to proceed slowly enough, for example, at lower temperatures, the precursor solution flow and thus amount of added ACC could be tuned to replicate even macroscopic templates.

The approach of Li and Qi^[16] is a significant step towards large 3D macroporous single crystals and combines several desirable features of an easy and versatile synthesis via amorphous precursor particles:

1. The synthesis procedure is straightforward and rapid and can be performed at room temperature with standard laboratory equipment and with cheap and commonly available chemicals.
2. No additives are required for the stabilization of the amorphous phase.
3. The size of the nanosized template is well below the critical 10–15 μm required for the synthesis of large micropatterned single crystals.^[15] The reported procedure can be applied to a number of other nano- and micropatterned templates, provided that vacuum can be used to infiltrate the template completely with the precursor.
4. Amorphous precursor phases are known for a large number of organic and inorganic crystals and are usually available through fast kinetic precipitation. The reported approach is facile and universal for many crystalline systems, provided that crystallization can be inhibited long enough for complete template replication by the amorphous precursor.
5. If the amorphous precursor phase can be kept metastable in the infiltrated template, an organized surface or seed

crystal with defined orientation towards the substrate can be used to nucleate crystals with defined orientation.^[17]

The resulting micro- and nanopatterned single crystals are promising for a number of applications, including various electronic, sensory, and optical devices. The application of amorphous precursor phases for the infiltration of an organic template with subsequent crystallization is an important transfer of biomineralization principles into the realm of synthetic materials. This gift from nature will certainly allow for a variety of exciting bottom-up approaches for the synthesis of future structured materials.

Published online: February 27, 2008

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