

Deposition of Structured Solids Using Templates
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Perhaps the most striking aspect of biological crystals is the range of incredible morphologies exhibited. An excellent example is provided by the sea urchin. While the skeletal plates and spines of this animal exhibit sponge-like microstructures, each is actually a single crystal of calcite (CaCO_3) (Figure 1). We are attempting to understand how biology controls crystallisation to produce such amazing morphologies, so these routes can be applied to synthetic crystal growth experiments.

While many synthetic techniques have been developed to control crystal growth, none approach the control achieved by biological systems. One of the principal differences between synthetic and biological crystal growth is that while the vast majority of synthetic experiments are carried out in bulk solution, precipitation of inorganic solids in nature almost without exception takes place within restricted volumes designed for this purpose.

We are currently using a number of model systems to investigate crystal growth within constrained volumes. CaCO_3 is being precipitated in the cylindrical pores of Track-etch membranes, which allows us to investigate how the pore size and chemistry affects factors such as the crystal polymorph, orientation, and morphology (1). This system also allows us to study the role of amorphous precursor phases in the formation of crystals, and we have shown that crystallisation of an amorphous solid within a restricted volume can be important in the morphological control of single crystals (Figure 2).

Irrefutable demonstration that a constrained volume can impose an external morphology on growing crystals was obtained by precipitating calcium carbonate in more complex moulds. Experiments have utilised sea urchin skeletal plates, from which a polymer replica is produced (2). Growth of calcium carbonate within these membranes produces either polycrystalline or single crystal particles, depending on solution concentrations. The single crystals are calcite and exhibit identical porous structures to the original polymer membrane (Figure 3). These experiments demonstrate that single crystals with complex form are within the grasp of synthetic chemistry.

As an alternative to growing crystals *de novo*, we are also producing structured inorganic solids by templating an existing biomineral. A range of techniques (such as electroless deposition) are being used to form macroporous replicas of sea urchin skeletal plates, in materials such as SiO_2 , Au (Figure 4) and Ni (3,4).

References

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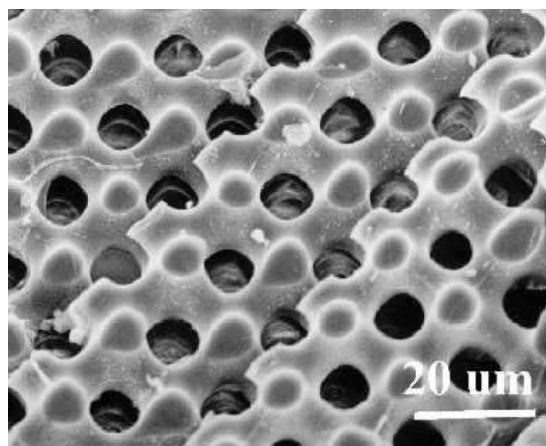


Figure 1: Microstructure of sea urchin skeletal plate

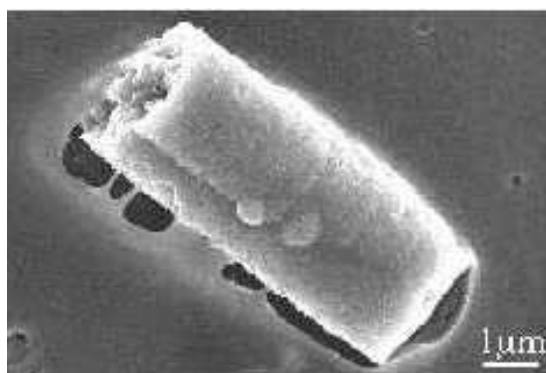


Figure 2: Calcite crystal grown in track-etch membrane pore

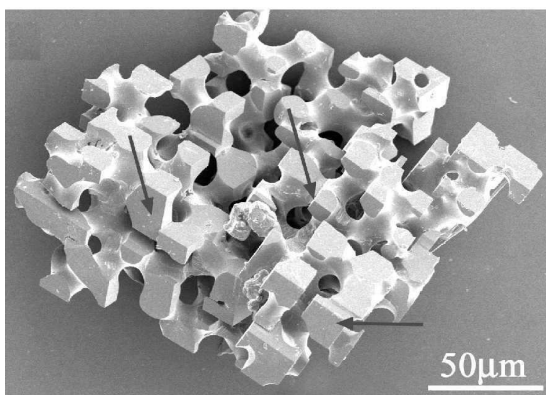


Figure 3: Single crystal of calcite grown in sponge-like membrane

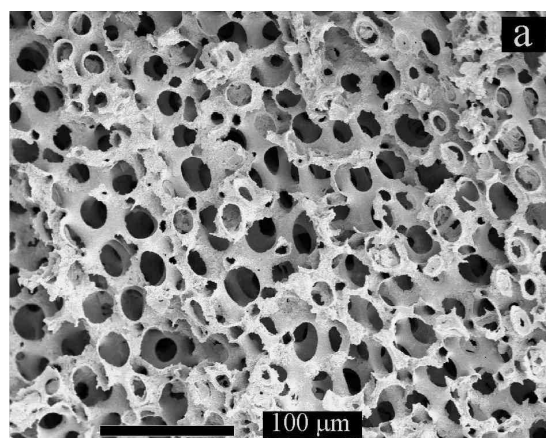


Figure 4: Macroporous gold produced by templating sea urchin plate