In a tight corner

Surfaces are known to act as catalysts for the nucleation of crystals. Using polymer films patterned with nanopores, it is now shown that the shape of the pores can control the kinetics of surface-induced crystal nucleation.

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The nucleation of a crystal in solution starts with a microscopic fluctuation, which usually occurs at an interface — for instance that at the container’s wall or between the solution and a solid impurity. Because of the small size of a crystal nucleus growing at a surface, most of the molecules in the nucleus are positioned at an interface, either that between the surface and the crystal, or the crystal–liquid interface that develops as the nucleus grows. Hence, as it is favourable that these interfaces are lattice planes, appreciating the role of the angle at which the surface–crystal and crystal–liquid interfaces meet — within a surface pore, for instance — is crucial to understanding the initial stage of surface-induced crystal formation. However, studying the effect of pore shape in experiments has been a challenge. Writing in *Nature Materials*1, Diao et al. report that nanopores in polymer films can promote the nucleation of aspirin crystals, but only if the pores have sides that meet at the correct angle. Their findings represent a significant advance in the ability to rationally engineer surfaces to control crystal nucleation.

The authors used state-of-the-art lithography to pattern a polymer surface with precisely shaped (round, square and hexagonal) pores 15–120 nm in size. After immersing the surface in a supersaturated solution of aspirin (that is, a solution with a higher concentration of aspirin than that at the solution–crystal equilibrium), the authors measured the average time needed for aspirin crystals to appear in the pores. They found that for a surface with square pores, this time was smaller by a factor of three than that for a flat surface of the same material, and that for hexagonal pores it was smaller by a factor of ten. Interestingly, they also observed that the crystals that grew in the pores were aligned with respect to the pore corners (Fig. 1).

It is not clear why crystal nucleation is fastest in the hexagonal nanopores. Although the different angles in square and hexagonal pores certainly affect nucleation rates significantly, in molecular crystals the rates are also sensitive to details on the ångström scale. The hexagonal and square pores investigated by Diao and co-workers1, although made in the same material, were fabricated by slightly different lithographic processes, and the surfaces may thus show differences on the ångström level that may contribute to variations in nucleation rates. Moreover, surfaces with controlled pore shapes can also be produced by other means, as previously shown by the preferential crystallization of one organic molecule along wedges formed by cleaving a single crystal of a different organic molecule2.

So, what is next? Fabricating surfaces with pores with nanometre precision is difficult. Indeed, for small molecules such as aspirin, the size of a nucleus at the initial stage of crystallization is typically a few tens of nanometres, and altering the shape of an angular nanopore by just a few degrees can change nucleation rates by more than an order of magnitude3. Moreover, if the only goal is to catalyse crystallization, the most efficient surfaces are porous, with pore sizes similar to that of the crystal nucleus, and disordered — that is, with a large variability in pore shapes and sizes. Indeed, porous, disordered surfaces can induce crystallization at lower solution supersaturations4,5 (lower concentrations of the crystallizing molecule). This is believed to be a consequence of the large number of nanopores of all sizes and shapes that disordered surfaces contain (Fig. 2a); the odds are that at least one pore will fit the crystalline nucleus perfectly. Nucleation then occurs rapidly in this pore. However, the nanoporous surfaces considered by Diao and co-workers only reduced the time for crystals to appear at a fixed supersaturation6, which is a weaker effect because nucleation rates sharply decrease with decreasing supersaturation.

Yet the authors’ lithography technique provides unprecedented control and flexibility over pore geometry, and this is a significant advantage over disordered surfaces. Indeed, as the authors point out, the ability to fabricate surfaces with pores of precise shapes potentially offers control over the crystal polymorph that nucleates. Although this has yet to be demonstrated, it is a much sought-after ability, in particular because of the need to control the polymorph that forms when making pharmaceuticals. The idea of using pore shape to catalyse the polymorph that nucleates is simple. Let us consider a liquid that can crystallize into two polymorphs, say cubic and triclinic. To nucleate the cubic polymorph under conditions that would normally produce the triclinic form, lithography could be used to make pores with right-angled corners.
Micelles in a crystal

Inclusion of organic molecules in inorganic crystals is thought to enhance their mechanical properties, yet obtaining high occlusion levels has been a challenge. It is now shown that synthetic calcite single crystals incorporating a significant amount of copolymer micelles have mechanical properties similar to biogenic calcite crystals.

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Synthetic efforts have identified a growing number of classes of organic (macro)molecular impurities — 1-nm dye molecules, 10–20-nm polymeric gel fibres and even 200-nm colloidal particles — that can be trapped within inorganic crystalline hosts such as calcite single crystals without significantly disrupting their crystalline lattices. Inclusion of an organic phase is believed to play a key role in enhancing the mechanical properties of the crystals, which are believed to share structural features with biogenic minerals and to have both increased hardness and fracture toughness relative to their pure, geological counterparts. However, the growth mechanisms of the single-crystal composites, the distribution of the organic phase and its effect on the resulting improved mechanical properties are poorly understood. Writing in Nature Materials, Kim et al. now report the synthesis of single crystals of calcite containing a considerable 13 wt% (approximately 30 vol%) of 20-nm anionic diblock copolymer micelles that have structural and mechanical properties analogous to those of natural biominerals (Fig. 1). The system should be an excellent model for further property characterization and for the study of growth mechanisms in biogenic minerals.

Using a variety of techniques, including X-ray diffraction and infrared spectroscopy, the researchers demonstrated that the incorporated micelles lead to an increase in the level of atomic disorder at the inorganic–organic interface and to a compressive-strain gradient in the calcite lattice. High-resolution transmission electron microscopy imaging of thin slices of the crystals revealed further details about their internal structure, in particular a preferred orientation of the micelles along a specific facet of the calcite crystals (in this regard, the presence of sticky and flexible carbonate units on the micelles’ surface is believed to play a critical role). Moreover, nanoindentation experiments demonstrated the crystals’ increased hardness with respect to geological calcite. Similar increases in hardness had also been observed for biogenic calcite crystals with occluded organic macromolecules; however, this enhancement is unprecedented in a synthetic crystal. The advantages of the synthetic system, such as the ability to vary systematically the volume fraction of the organic phase, will certainly lead to further insights into the hardening mechanism, which remains to be fully understood.

The incorporation of organic materials into a crystal host is a non-equilibrium process that strongly depends on kinetic, entropic and enthalpic constraints, as well as on physicochemical variables, including the occlusions’ size, shape, surface chemistry and (possibly) rigidity. In addition, the properties of the host crystal need to be taken into account. As established by earlier work with smaller additives, near-equilibrium crystal growth rates are sufficiently slow that the chemistry of the additive material is a key factor in determining its crystallographic location and orientation. More recently, larger materials, such as polymers and proteins, have also been shown to be selectively incorporated onto specific crystal facets. For these systems, experiments with in situ atomic force microscopy are unravelling...