



Figure 2 | Nucleation of crystals (red) in porous surfaces (pores, white; surface, grey). **a**, In a disordered, porous or pitted material, the large variety of pore sizes and shapes makes it highly probable that the nucleus of any polymorph will fit almost perfectly into at least one pore. **b**, In square pores, a cubic crystal is expected to nucleate faster than a triclinic polymorph (which has no right angles) because a cubic nucleus better fits into the right-angled corners of the square pores.

to fit the nucleus of the cubic polymorph (Fig. 2b). Conversely, the nucleus of a triclinic crystal would be a poor fit to pores with right-angled corners because the crystal would need to incorporate either strain or defects. As a consequence, right-angled pores

should selectively favour nucleation of the cubic polymorph.

Another application of nanopatterned surfaces may be found in surface-induced ice nucleation. On the basis of work on rough surfaces, such as those of typical atmospheric

microparticles, it has been assumed that water droplets in contact with a surface start to freeze from the edge of the droplet — that is, along the contact line. However, recent experiments on very smooth surfaces have indicated that nucleation occurs away from the edge of the droplet⁷. Lithography-produced surfaces such as those of Diao and colleagues¹ may offer a way to resolve this apparent contradiction. □

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BIOMINERALIZATION

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.

Lara A. Estroff and Itai Cohen

Synthetic efforts have identified a growing number of classes of organic (macro)molecular impurities — 1-nm dye molecules¹, 10–20-nm polymeric gel fibres² and even 200-nm colloidal particles^{3,4} — 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^{5–7} 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*⁸, 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 carboxylate 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 macromolecules⁵; 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 orientation¹. More recently, larger materials, such as polymers and proteins, have also been shown to be selectively incorporated onto specific crystal facets^{6,7,9}. For these systems, experiments with *in situ* atomic force microscopy are unravelling

the underlying mechanisms leading to the observed morphology, including various instabilities in the crystal growth front when macromolecules bind to step edges¹⁰. However, as the size of the additive increases beyond the dimensions of the unit cell of the host crystal, the role of surface chemistry seems to diminish and incorporation becomes significantly less dependent on the specific crystal lattice. For example, when either carboxylate-functionalized polymer particles (200–250 nm) or neutral agarose hydrogel fibres (10–20 nm) are trapped within single crystals, incorporation is random along the crystallographic directions^{2–4}. In the context of those studies, the inclusion of 20-nm anionic micelles achieved by Kim and colleagues⁸ is surprising. Despite the fact that they are similar in size to the hydrogel fibres and in surface chemistry to the polymer particles, the micelles selectively adsorb on specific crystal facets. This result shows that the right combination of surface chemistry, size and rigidity can lead to the oriented incorporation of objects larger than previously thought possible. However, further understanding of the interplay of the relevant factors involved in the mechanism of incorporation, including the kinetic competition between crystal growth and adsorption of organic material¹⁰, is needed to determine design criteria for the pairing of host crystals with occlusion materials that achieve a desired degree of inclusion and crystallographic selectivity.

In the future, bio-inspired synthetic approaches such as that of Kim and co-authors⁸ could be used to tune the mechanical properties of inherently brittle inorganic single crystals and to obtain a better understanding of the microscopic origin of the enhanced mechanical properties of the organic–inorganic composites. We foresee the application of synthetic

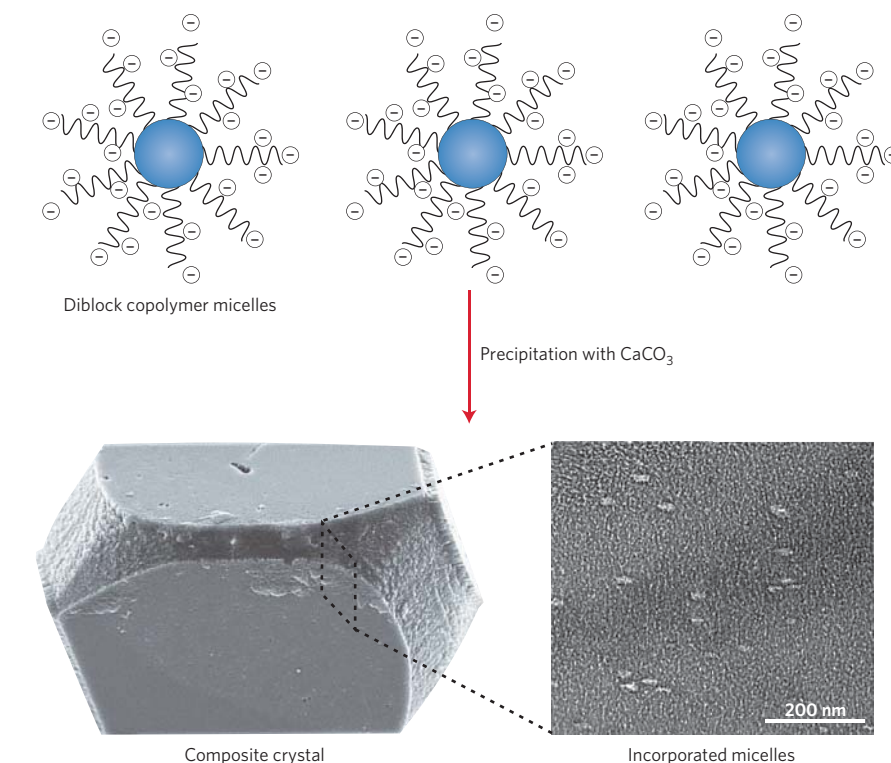


Figure 1 | Inclusive crystallization of micelles within calcite single crystals⁸. When calcite crystals are grown in the presence of anionic diblock copolymer micelles, the micelles become trapped within the final structure. On incorporation, the originally spherical micelles become ovoid (transmission electron microscopy image, bottom right) and align along a specific crystallographic direction.

approaches to a variety of host crystals and occlusion materials with electronic, photonic or magnetic properties, eventually leading to functional, nanostructured, single-crystal components. □

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QUANTUM INFORMATION

Noisy neighbours under control

The ability to control the nuclear spins in a semiconductor quantum dot is an important step towards a long-lived and controllable electron spin qubit.

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The solid state has been the arena for numerous demonstrations of quantum mechanical effects. Lately, coherent control of single quantum systems has been achieved in a variety of systems, including single atoms and photons, as well

as solid-state systems. One example of a two-state quantum system is the spin of an electron, which constitutes an interesting realization of a quantum bit (qubit)¹. In solid state, the interaction between two qubits can typically be made strong rather

easily, which is a big advantage if one aims to construct a quantum information processor. The disadvantage, however, is that solid-state qubits tend to interact with a high number of other particles in their environment, which essentially results in