

ADVANCED MATERIALS

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Bioinspired Polymer–Inorganic Hybrid Materials**

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Biominerals provide a unique inspiration for materials design,^[1] as illustrated by Nature's ability to manipulate poor engineering materials such as calcium carbonate to produce skeletal materials with considerable fracture resistance.^[2,3] Under biological control, the rhombohedral single crystal of calcite becomes bicontinuous and spongelike in morphology when produced as the skeletal plates of echinoderms. Biominerals are typically composite materials, being intimately associated with organic macromolecules and exhibiting a hierarchical organization on length scales ranging from the nanometer to the macroscopic level.^[4,5] As a consequence of the hybrid composition and the structural organization, the mechanical properties of many biominerals are superior to synthetic crystals.^[6] Mollusc nacre, for example, displays considerable stiffness, strength, and toughness and is 3000 times more fracture resistant than a single crystal of pure aragonite.^[7] This can be attributed to its structure.^[8,9] The aragonite tablets in abalone nacre exhibit a stacked structure in which the crystallographic axes of all crystals within the stack are coaligned and adjacent crystal layers are separated by organic sheets.^[2,3] Contrary to the long-accepted opinion that the crystallographic alignment is directed by the organic matrix, it has recently been shown that each of the aragonite stacks is in fact a single crystal, whose growth proceeds via mineral bridges through pores in the interlamellar organic sheet.^[10] These organic sheets have been shown to contain pores 20-100 nm in diameter.

Organic matrices are fundamental to crystal-growth control in vivo. In addition to creating the unique environment in which mineralization occurs, functionalized matrices can also define the location and crystallographic orientation of crystal nuclei.^[11,12] Synthetic model matrices such as Langmuir monolayers^[13–16] and self-assembled monolayers (SAMs)^[5,17,18] have been successfully used to mimic biological control by an organic matrix over crystal orientation. A more sophisticated level of control can be achieved using patterned SAMs to define the location of nucleation sites and direct the formation of ordered arrays of crystals.^[17,18]

Both of these techniques, however, suffer a number of limitations, as they are, for example, inflexible in terms of preparation technique and they offer patterning on a limited length scale only. We report here a simple and general approach to matrix-mediated crystal growth, employing structured films of generic polymers to direct the growth of crystals. By using straightforward patterning techniques we are able to access a continuous range of length scales ranging from the macroscopic to the nanometer level. Further, in contrast to SAMs, polymer films can be selectively lifted off a supporting substrate and thereby fully embedded into the inorganic matrix during crystal growth. Crystallization initiated on a nanostructured polymer film not only provides easy access to unprecedented length scales (as small as 10 nm), but, for the first time, offers an organic film that is structurally very similar to an organic matrix directly involved in biomineralization, that is, organic sheets separating the aragonite tablets in abalone.^[10]

Polymer templates comprising 120 nm thick films of poly(styrene) (PS) or poly(vinyl pyridine) supported on silicon wafers and patterned with regular arrays of circular holes, grid patterns, and parallel lines ranging in size from 10 µm to 500 nm were prepared using nanoimprint lithography. Calcite crystals were grown on these surfaces either by immersion of the substrates into a supersaturated solution of CaCO₃^[19] or using an ammonia diffusion method,^[20] and similar-sized crystals of approximately 50 µm were obtained in each case, with the diffusion technique tending to produce somewhat larger crystals. Both types of polymer films also gave identical results and supported the growth of non-oriented, regular rhombohedral calcite crystals. Although the macroscopic form of the crystals was not significantly affected by the structure of the polymer film, examination of the crystal face in direct contact with the polymer substrate revealed perfect replication of the polymer pattern in the morphology of the nucleating crystal face. Figure 1a shows an image of the nucleating crystal faces of calcite crystals grown on a PS thin film patterned with 1 µm wide holes. The nucleation faces display a regular array of 1 µm wide posts that perfectly correspond to the pattern of the polymer template.

Similar results were obtained from crystal growth on polymer films patterned on the micrometer scale with a range of structures (Figs. 1b–f). Figure 1b shows a stripe pattern, while a mixed ordered/random pattern is shown in Figure 1c and d. An interesting example is presented in Figure 1e, where the polymer template was in a grid pattern comprising $1 \,\mu m$

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Figure 1. Scanning electron microscopy (SEM) images of calcite crystals grown via the ammonia-diffusion technique for 12–15 h on thin PS films that were prepared by nanoimprint lithography. a) The nucleation faces of the crystals are patterned with an array of 1 μ m wide posts, as directed by the polymer template, which consisted of a regular array of 1 μ m wide holes. The inset shows a higher magnification of the posts. b) Calcite crystal face patterned with stripes. c,d) Top and bottom view of crystals grown on a combined pattern with irregular large and regular small features. e) Calcite crystal with the polymer grid pattern still attached to the crystal face, f) shows a magnification of this feature: The outgrowths show preferred facets which are coaligned with the parent crystal. This is an indication that the parent single crystal continued growing through the polymer template.

squares, and where the polymer grid remained adherent to the crystal face. In this case, crystal growth occurred through the polymer film and then continued laterally to give outgrowths extending beyond the confines of the polymer pattern. Figure 1f shows a magnification of this feature, demonstrating that the crystallographic faces of these outgrowths lie parallel to the external faces of the parent crystal. The pattern formed on the nucleating crystal face therefore represents a continuous extension of the parent crystal and the entire structure is a single crystal.

The flexibility of our experimental approach was further exploited to produce thin polymer films with different pattern morphologies and length scales. Access to polymer films with much smaller feature sizes was provided by a simple spin-casting procedure. Polymer templates with lateral feature sizes ranging from 100 to 10 nm were prepared by demixing of mixtures of low-molecular-weight PS and poly(methyl methacrylate) (PMMA) during spin-casting. Subsequent dissolution of the PMMA generated a porous PS film approximately 90 nm thick in which the holes range from 10 to 50 nm in diameter^[21] (Fig. 2a).

Rhombohedral calcite crystals were again grown on the patterned substrate using the metastable solution method and translation of the polymer-film pattern into the nucleating crystal face was observed. Interestingly, the change in pattern of the polymer film from an array of micrometer-sized circular holes to a nanometer-scale porous network had a significant effect on the product crystal morphology. Examination of the crystal face in direct contact with the polymer substrate revealed an intimate association between the inorganic and organic phases. Subsequent to crystal nucleation on the top surface of the polymer film, growth then continued into the pores of the polymer film, as shown in Figure 2b–d, where the nucleation face of a rhombohedral calcite crystal exhibits a nanoscale pattern. When lifting the crystal from the substrate, the polymer film typically adhered to the crystal, indicating



Figure 2. Crystal growth on a PS template with 10-50 nm pores. a) SEM image of a porous PS film prepared by phase separation during spincoating of a PS-PMMA blend and selective removal of the PMMA [21]. b-d) Calcite crystals grown from a supersaturated solution grown for 12-15 h on the surface of the polymer film. The images show the nucleating crystal faces which are revealed by lifting the crystal off the substrate. b,c) Polymer film adhered to these faces. After removal of the polymer, the templated growth of the crystal is visible in (d). The facets of the crystal protrusions (arrows) are coaligned with the macroscopic crystal, indicating that they represent continued growth of the parent single crystal.



better adhesion of the polymer film to the calcite crystal than to the silicon wafer. Some parts of the polymer film, however, detached from the crystal surface, revealing the patterned crystal face (arrows in Fig. 2b and c). The size and shape of the features patterned in the crystal face correspond to the 10–50 nm pores in the polymer film, conclusively demonstrating the templating role of the polymer. That growth through the pores in the polymer represents a continued growth of the parent calcite crystal is supported by the observation that many of the protrusions into the polymer have regular facets that are coaligned with faces of the macroscopic crystal, indicating that the entire structure is a single crystal (Fig. 2d).

Remarkably, crystallization again did not terminate once the pores in the polymer film had been filled, but continued on the opposite side of the film, producing a sheetlike crystal linked to the parent crystal through mineral bridges spanning the entire thickness of the polymer film (Fig. 3). The polymer film therefore becomes fully encapsulated within a single crys-



Figure 3. Encapsulation of the organic template into the crystal. Calcite crystal grown from a metastable solution overnight. The growth of the crystal proceeded through the pores of the organic matrix and continued laterally on the opposite side of the PS film. a) SEM image of the crystal surface which formed in contact with the substrate. {104} faces are clearly visible (arrows). b) Side view of the marked area in (a), clearly showing encapsulation of the structured polymer film. The structure in (a) and (b) consists of crystalline bridges linking the single crystals on both sides of the film. The identical orientation of these two crystals confirms that the entire structure is a single crystal.

tal of calcite, producing a hybrid inorganic–organic material. The morphology of the newly formed layer fully supports our single-crystal growth model in that the lamellar crystal overgrowth shows internal {104} facets that are coaligned within the area itself and with the external faces of the macroscopic crystal. This is also unambiguously shown in Figure 1e and f, where a micrometer-scale template is used. A schematic diagram of the processes leading to Figures 1 to 3 is shown in Figure 4.



Figure 4. Schematic diagram of the template-modified crystal growth. a) Starting from a structured polymer film, b) calcite crystals nucleate on the top surface of the polymer film and start to grow into the pores in the film, c) resulting in translation of the polymer-film structure into the nucleation face of the single crystal. d) Lift-off of the polymer film from the substrate enables further crystal growth on the opposite side of the polymer, resulting in encapsulation of the polymer inside the single crystal. For clarity, the portion of the crystal that sits on top of the polymer film is rendered partially transparent.

For this process to occur, lift-off of the polymer film from the substrate must take place during crystallization, such that the polymer film becomes encapsulated within the crystal. The polymer must therefore adhere better to the growing crystal face than to the silicon wafer substrate. That crystal growth proceeds after emerging from the polymer pores is fascinating, since it occurs on the crystal surface adjacent to the substrate. This process relies upon adequate ion transport to this crystal face, which in turn requires sufficient physical separation between the majority of the crystal face and the substrate. This is achieved through polymer lift-off from the substrate. Additionally, when the thin polymer films are detached from the substrate, as occurs during lift-off, they are intrinsically too weak to hold the crystal in place on the silicon wafer during removal of the sample from solution for analysis. That the patterned crystals remain in their original position on the substrate strongly suggests direct adhesion of some areas of the crystal nucleation face to the silicon wafer in the product crystals. A detailed investigation of this process is underway.

Structured polymer films provide a versatile new route to patterning crystal growth and generating inorganic–organic hybrid materials. While a number of techniques have been used previously to pattern the gross morphology of calcite single crystals, including growth in lithographically created moulds,^[22] templates derived from biominerals,^[23,24] or on col-





Crystallization of CaCO₃ on Polymer Substrates: CaCO₃ was grown on the patterned polymer substrates from either a supersaturated CaCO₃ solution [19], or using the ammonia difuusion technique [20]. Metastable solutions were prepared by freshly mixing equal volumes of 0.4 M CaCl₂ and 0.4 M Na₂CO₃ solutions. A substrate was placed into the solution and crystal growth was allowed to proceed for 15 to 20 h. This yielded calcite single crystals with a diameter of approximately 50 µm. For the diffusion technique, a substrate was placed into a 0.4 M CaCl₂ solution, which was placed into a sealed desiccator that also contained a vial of solid ammonium carbonate. After 12 to 15 h 50–100 µm sized single calcite crystals had formed on the substrate.

Imaging Techniques: The CaCO₃ crystals were characterized using scanning electron microscopy (SEM). The substrates were either directly mounted onto a SEM sample support, or in order to image the face in contact with the polymer film, the crystals were lifted from the silicon substrate using adhesive carbon tape, which was then mounted on an SEM sample support. The samples were sputter-coated with Pt–Pd and imaged using a JEOL 6330 FEGSEM operating at 10 kV and a Leo field-emission scanning electron microscope, LEO 1530 operating at 5 kV.

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significantly more flexible and general. By accessing a wide variety of patterning techniques and matrix materials, use of structured films of generic polymers to direct the crystal growth provides a procedure that incorporates the organic phase into a growing single crystal and spans a wide range of pattern sizes and periodicities. In this communication we have shown that growth of a single crystal occurred through the pores in a nanostructured polymer film and that the organic layer was incorporated within the crystal. This is directly analogous to the mechanism proposed for nacre formation in abalone, in which each stack of aragonite tablets is a single crystal which extends through pores in the organic sheet separating adjacent plates in the stack. Our polymer template is very similar—both in shape and size—to the organic matrix extracted from the biomineral by Schaeffer et al.^[10]

loidal particle monolayers,^[19] the method described here is

In summary, we reported here a novel route leading to a synthetic polymer–inorganic composite material with a structure that closely resembles abalone nacre. Our experiments also demonstrate that the growth of a single crystal can be controlled with a precision of 10 nm. It is also envisaged that our approach could be readily extended to employ three-dimensional scaffolds. A three-dimensional porous organic monolith could be used to create materials that have a bicontinuous organic/crystal morphology in three dimensions. Block copolymers, for example, can provide access to macroscopic samples with patterns on the 10 nm level. Our methodology is also quite general and could be applied to many other inorganic crystals produced under ambient conditions.

Experimental

Nanoimprint Lithography: All experiments were performed using an Obducat nanoimprinter. Thin PS (weight-average molecular weight, $M_w = 100 \text{ kg mol}^{-1}$) and poly(2-vinyl pyridine) (P2VP, $M_w = 100 \text{ kg mol}^{-1}$) were spin-cast from 2 wt % toluene solutions onto snowjet-cleaned [25] silicon wafers resulting in film thicknesses of approximately 120 nm. Silicon wafers with micrometer-sized topographic structures were used as masters. Prior to use, masters were rendered hydrophobic by deposition of a ${}^{1}H^{1}H^{2}H^{2}H$ -perfluorodecyltrichlorosilane (Fluorochem, 97%) SAM in order to avoid the adhesion to the polymer. The master was then placed in face-to-face contact with the polymer sample, loaded inside a hydraulic press, and heated to 150 °C, which is above the glass-transition temperature of PS and P2VP. A pressure of 40–60 bar (1 bar = 100000 Pa) was applied for 5 min to transfer the pattern into the polymer film. The polymer was solidified by cooling before removing the master.

Nanophase Separation of Polymer-Blend Films: Thin polymer-blend films were prepared by spin-coating 2 wt % solutions of mixtures of PS ($M_w = 10.7 \text{ kg mol}^{-1}$, $M_w/M_n = 1.02$) ($M_n =$ number-average molecular weight) and PMMA ($M_w = 10.0 \text{ kg mol}^{-1}$, $M_w/M_n = 1.07$) from tetrahydrofurane onto snowjet-cleaned silicon wafers. The volume ratio of PS to PMMA was 3:7. The thickness of the film was approximately 150 nm, measured using ellipsometry and atomic force microscopy. The films were immersed in glacial acetic acid for several minutes to dissolve the PMMA component. This yielded an approximately 90 nm thick structured PS film with 10–50 nm wide pores (Fig. 2a). Atomic force microscopy imaging was used to verify that the polymer layer consisted of a PS matrix with pores that expose the surface of the silicon wafer. Since the M_w of PS was below the entanglement molecular weight the resulting film was mechanically fragile.