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Templated Nucleation in a Dynamic Environment: Crystallization in Foam Lamellae

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The understanding of biomineralization processes, molecular recognition, and structural aspects of crystal nucleation and growth have opened up significant opportunities in the world of materials science.[1−7] It has been known for many years that crystal morphologies can be controlled by use of specific additives,[2,3] but only recently has it been discovered that the segregation (e.g., as monolayers) of amphiphilic molecules at the air/solution interface can be effective in controlling three-dimensional nucleation in supersaturated subphases. The control of polymorphic form, crystal size, and orientation of calcium carbonate precipitating from aqueous solution have been demonstrated[8,9] as has[10−12] the catalyzed nucleation of α-glycine as {010} pyramids and plates.

Large-scale application of this elegant work has not yet been realized since the technique relies on the nature of the interface between monolayer and supersaturated subphase for its viability. Until now this has only been demonstrated on a small scale in static systems. To exploit this scientific discovery as novel process technology for the preparation of nanophases or specifically oriented materials two further issues have to be resolved: first the process productivity must be increased via the interfacial area/unit volume of solution, and second the nucleating properties of the interface (templating) must be maintained under the dynamic conditions likely to be encountered on a large scale. We report here how the liquid film lamellae in a foam may be successfully used as a means of simultaneously fulfilling these criteria. A foam provides a high surface area of gas bubbles dispersed in a liquid. The stabilizing surfactant or other amphiphile adsorbs at the gas/liquid interface and hence offers the possibility that the liquid lamellae might be used as locations for templated crystallization. Since the thickness of these liquid lamellae are controlled by drainage within the plateau borders of the foam,[13] it also follows that the size of resulting crystals may be controlled via the drainage rate. To test these hypotheses, we have utilized the templated crystallization of calcium carbonate and glycine referred to above.

Analytical reagent grade chemicals were used directly without further purification: glycine, leucine, α-aminooctanoic acid, polyoxyethylene ether (Triton X-405 and $C_{12}E_5$), arachidyl (C_{20}) sulfate, and calcium chloride from Sigma Chemicals, sodium hydrogen carbonate from Fisons, and *n*-hexadecyl (C_{16}) sulfate from Lancaster Synthesis.

In the case of glycine, supersaturations (0.02−0.25) were imposed by cooling aqueous solutions of known composition.[12,14] Stable supersaturated solutions[15] of $CaCO_3$ (4.36 at 25 °C, pH 8.1) were prepared by dropwise addition of 0.01 M $NaHCO_3$ to 0.01 M $CaCl_2$.

In-situ experiments at the air bubble/solution interface were performed to check our methodology against previous work[10,11] and to confirm the occurrence of oriented nucleation at a bubble surface. A drop of hot unsaturated glycine solution containing dissolved leucine, Triton X-405, and an air bubble was placed between two glass slides and then cooled naturally to room temperature. Crystallization was monitored by an optical microscope (Polyvar).

Crystallization in foams was carried out in a cylindrical jacketed vessel of capacity 2 L (20 cm in height and 6 cm in diameter). Foams were produced by a foaming homogenizer (Ultra-Turrax, TP 18−10) used in conjunction with compressed air and an added surfactant or amphiphile. Foam heights were measured as an indication of foam stability. Bubble diameters were in the range of 0.5−2.0 mm.

Morphological observations and crystal size measurements were made by optical microscopy (Polyvar-Mat) and scanning electron microscopy (SEM, Hitachi S-520). Polymorphic forms and morphologies of precipitates were categorized using optical two circle goniometry (STOE-J) and X-ray powder diffractometry (Scintag 2000).

When grown in the presence of surfactant-stabilized air bubbles, glycine crystals appeared as bipyramids in the bulk of solution rather than at the air bubble/solution interface (Figure 1a). In contrast, in the presence 6 mg/mL (*R*)-leucine Figure 1b shows the development of pyramidal glycine crystals templated on (010) faces at the air bubble/solution interface. Figure 1c shows a similar experiment in the presence of 6 mg/mL racemic leucine in which rhombic {010} plates form due to the presence of both enantiomers in the solution. Overall, this oriented nucleation results from the prochiral nature of the {010} faces and the enantioselective occlusion of the additive isomers along the *b*-axis and is consistent with earlier reports.[11] These observations confirm that the templated nucleation observed previously in static experiments is likely to be mimicked at the air/solution interfaces in foams and also indicate that the crystal morphology may be used as an indicator of the nucleation site with bypyramids reflecting nucleation in bulk solution and {010} pyramids and plates indicative of templated nucleation at the air/solution interface.

The experimental data recorded in the crystallizations from foams are summarized in Table 1. A number of points are worth emphasising. First, when glycine grew in the liquid layers of foams stabilized by α-aminooctanoic acid or leucine, the induction time for nucleation was reduced[16] and crystals of pyramidal and platelike morphology formed, consistent with a templated nucleation process within the liquid layers of the foam. Second, when the nonionic surfactant was used alone, the crystal morphology was bipyramidal typical of nucleation from bulk solution but when

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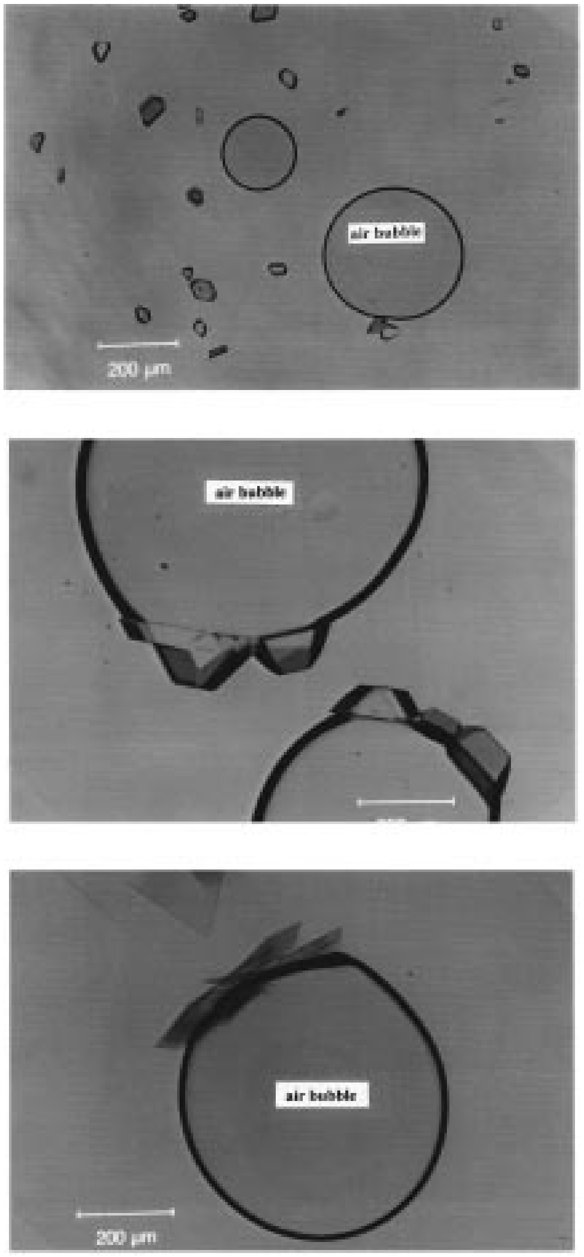

Figure 1. Glycine crystals grown at the air bubble/solution interface stabilized by (a) 200 μM Triton X-405, (b) 6 mg/mL (*R*)-leucine,(c) 6 mg/mL (*R*,*S*)-leucine.

Table 1. α-Glycine: Summary of Experimental Results

system	crystal morphology at air/solution interface	crystal morphology in foam	mean cryst size[a]	effective foam height[b]	induction time[c]
glycine	bipyramid	bipyramid	200	0	1500
glycine + (*R*)-leucine	pyramid	pyramid	90	4	360
glycine + (*R*,*S*) α-amino-octanoic acid	{010} plates	{010} plates	80	12	450
glycine + Triton X-405	bipyramid	bipyramid	50	35	18000
glycine + (*R*)-leucine + Triton X-405	pyramid + bipyramid	pyramid + bipyramid	45	24	8500
glycine + (*R*,*S*)-α-amino octanoic acid + Triton-405	{010} plate + bypyramid	{010} plate + bipyramid	40	30	12000

[a] $S = 0.10$, in μm. [b] At total amount of 200 μM surfactant (in cm). [c] For nucleation at $S = 0.05$, in seconds.

used in conjunction with these amino acids a mixture of bipyramids, pyramids, and {010} plates were produced indicating partial templating. Finally, crystals grown in the liquid layers of the foams are significantly smaller than those grown under monolayers at a comparable supersaturation. At the air/solution interface in a crystallizing dish, crystals are typically from 0.5 to 1.0 mm while from a polyhedral foam crystals as small as 10 μm are formed. These experimental results indicate that the thickness of the liquid layers of a stable foam can be used to restrict the size of product crystals.

In the case of calcium carbonate, three polymorphs—calcite, vaterite, and aragonite—are often found in crystallization from aqueous solution.[17] The specific form depending on the crystallization conditions (temperature, supersaturation, pH, ionic strength, and the presence of additives). Calcium carbonate grown in the liquid layers of foams stabilized by 20 μM $C_{12}E_5$ was found to be 100% vaterite with a crystal size of about 5 μm. In complete contrast, the addition of 20 μM *n*-hexadecyl sulfate to the $C_{12}E_5$-stabilized foam yielded crystals of a similar size which were 100% rhombic calcite. The same level of arachidyl sulfate gave a calcite/vaterite mixture. This result is consistent with the templating of the nucleation process as manifest by a change in polymorphic form of the product crystals and the previous study of Mann et al.[9] The difference in calcite templating between *n*-hexadecyl sulfate and arachidyl sulfate is thought to be due largely to the decrease in its water solubility which makes it less available at the air/water interface.

It is evident for both systems studied that the results of nucleation experiments carried out under self-assembled monolayers of appropriately designed amphiphiles can be transferred to a dynamic foam-based process. For both systems studied, the process of templated nucleation within the liquid layer of a foam has been demonstrated. Clearly, the most important feature enabling the general operation of this process is the availability of templates which give on one hand good foam stability and on the other are appropriately designed to template the nucleation process. In contrast to experiments carried out under monolayers where liquid-phase solubility is undesirable, a foam-based process requires that these additives must exhibit some solubility in the crystallizing medium in order to display the necessary surface activity. The work reported here has shown that it is possible to achieve the desired combination of properties by use of synergistic surfactant/additive mixtures. This is likely to be a successful solution since the molecular features which lead to self-assembly and templating at the air/water interface (e.g., hydrophobicity) are unlikely to be compatible with good liquid-phase solubility.

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