A new strategy for preparing macroporous materials: using a colloidal gas aphron to create an oriented crystal network

R. J. Davey, H. Alison, J. J. Cilliers and J. Garside

Colloids, Crystals and Interfaces Group, Department of Chemical Engineering, UMIST, Manchester, UK M60 1DQ. E-mail: r.j.davey@umist.ac.uk

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We report a simple and generic means of using a static colloidal foam to create a novel porous material, having porosity on the micrometer size scale, that arises from the creation of an oriented crystal network.

The development of materials science over the last decade owes much to our increased understanding of the structural and stereochemical factors which drive molecular recognition[1] processes in the creation of such supramolecular assemblies as crystals,[2] surfactant structures,[3] and colloidal aggregates.[4,5] This progress has been stimulated by the desire to understand and mimic biomineralisation phenomena,[6] to control morphology and polymorphic form of molecular solids,[7] and to synthesise a new generation of functional materials having nanoscale dimensions.[8] One particularly elegant example of this progress has been the discovery that monolayers of amphiphilic molecules at the air/solution interface can be effective in templating nucleation in supersaturated subphases. Thus, for example the control of polymorphic form, crystal size and orientation of calcium carbonate precipitating from aqueous solution have been demonstrated[9] as has[10,11] the catalysed nucleation of α-glycine as {010} pyramids and plates.

The application of this work either for large scale manufacture of particulate products or in the preparation of novel materials has hardly been addressed,[13] largely because it relies on the use of a small scale, static interface between templating monolayer and supersaturated subphase for its viability. In an attempt to demonstrate the potential of this scientific discovery in the preparation of materials we carried out the preliminary experiments reported here in an attempt to make a macroporous material. Control of porosity in the size range 1–100 nm has been demonstrated previously[15,16] but we believe the work reported here to be the first to address porosity in the micrometer size range.

The concept underlying this innovation is that since a foam consists of a high surface area of gas bubbles dispersed in a liquid then, with amphiphilic molecules located at the bubble surfaces, the liquid lamellae separating the bubbles might be used as locations for templated crystallisation. In experiments with single air bubbles in supersaturated glycine solutions we showed previously[12] that, in the presence of an amphiphile chosen to template the nucleation of glycine [*e.g.* (*R*)-leucine[10]] and a surfactant appropriate for stabilising a foam, it was possible to encapsulate a bubble with a crystalline layer of (010) oriented glycine crystals. This oriented nucleation results from the prochiral nature of the {010} faces and their stereochemical relationship to (*R*)-leucine, which segregates at the air/solution interface: it is consistent with earlier reports.[10,11] If this effect could be reproduced throughout the bulk of a stable static foam then it should be possible to utilise such a methodology to create a three dimensional material which has pore sizes corresponding to the bubble size of the foam and a network of solid walls composed of an interconnected array of ordered microcrystals. Such a process is shown schematically in Fig. 1.

In order to realise this concept we first created a colloidal gas aphron. This was achieved following the experimental method of Sebba[13] together with a combination of stabilising surfactant and nucleation inducing template molecules. Thus, for example, a solution of glycine containing 200 μM of either surfactant or a 50 : 50 wt% surfactant/template mixture was prepared at 60 °C and agitated, so as to entrain air, for 15 min at 4500 rpm. This produced a gas aphron with bubble sizes between 10 and 30 μm and 90% volume fraction of air, which under static conditions was stable for *ca.* 1 h. Cooling of this foam then initiated supersaturation and subsequent crystallisation of the glycine. We found that TTAB [$CH_3(CH_2)_{13}N(CH_3)_3Br$] was a particularly effective surfactant for stabilising these aphrons while the hydrophobic α-amino acids (*R*)-leucine and (*R*,*S*)-norleucine were used to template the nucleation at the bubble surface.[11] Control experiments were also carried out in which glycine crystals were prepared by cooling a bulk saturated solution of glycine containing the surfactant mixture. These gave crystals with an (010) plate morphology, as expected from previous work.[10]

When crystallised within the stable aphron containing a templating molecule, glycine was found to nucleate at temperatures between 8 and 15 °C higher than in corresponding bulk solutions (the value depending on the level of supersaturation which varied[12] between 1.01 and 1.20 at 25 °C) indicating that nucleation was catalysed. It was observed that almost no three dimensional growth took place within the bulk solution: glycine crystals grew around and out from the air-solution phase boundaries. This led to the formation of a 'solid foam', consisting of an interconnected glycine crystal network. As crystallisation proceeded a point was reached at which the gas aphron collapsed and liquid drained to the bottom of the sample. This left a 'skeleton' comprising a solid framework of oriented glycine crystals with pore sizes identical to, or slightly larger than, the original aphron bubble sizes. This is seen in

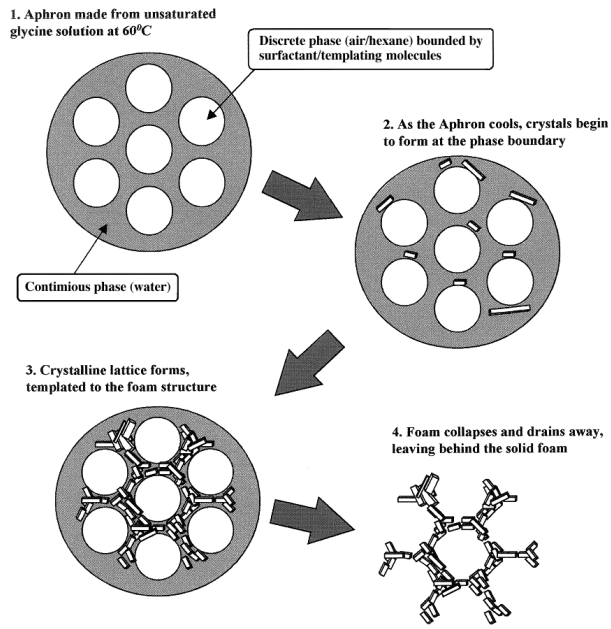

Fig. 1 Schematic depiction of crystallisation in a gas aphron showing the creation of an oriented crystal network and solid foam.

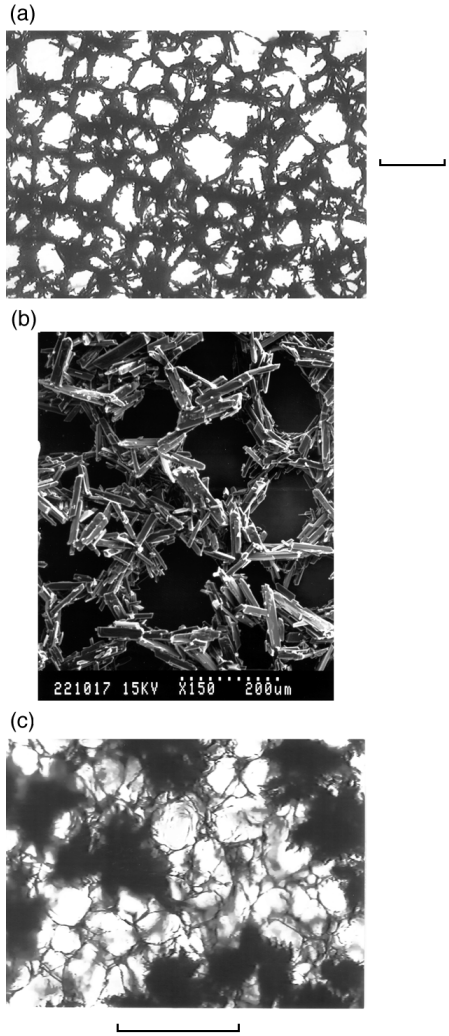

Fig. 2 α-Glycine crystal networks in solid foams prepared from supersaturated aqueous solutions of glycine in a gas aphron using TTAB as a stabilising surfactant and (*R*)-leucine [(a) and (b)] and (*R*,*S*)-norleucine as templating molecules: (a) templated by (*R*)-leucine, an optical micrograph (scale bar 150 μm), (b) templated by (*R*)-leucine, a scanning electron micrograph, (c) templated by (*R*,*S*)-norleucine, and optical micrograph (scale bar 100 μm).

Fig. 2(a), an optical micrograph, and Fig. 2(b), an electron micrograph. Crystals of sizes between 10 and 50 μm are oriented with their (010) facets bounding the pores. Two further observations were evident from the work. Firstly, crystallisation from a stable aphron was not in itself sufficient to create this microstructure: if the templating molecule was not present the oriented nucleation was lost and the foam and crystals collapsed to an unoriented powder. Secondly, when the templating molecule was present as a racemic mixture [(*R*,*S*)-norleucine in this case] not only were crystals templated with (010) orientation but growth was also inhibited in both directions along the *b*-axis yielding thin plate-like crystals. As seen in Fig. 2(c) this again forms a solid foam but now with significantly thinner walls.

It is our belief that this surprisingly simple experimental methodology may now be extended, not only to other solid phases such as fats, waxes, or inorganics but also to employ alternative disperse phases.[14] For example, we performed a preliminary experiment crystallising glycine from aqueous solution in the presence of hexane as the dispersed phase. In this case the size scale of the final crystal network can be reduced since oil drops in the size range 0.1–10 μm may be stabilised and it appears that the oil droplets themselves may be encapsulated by the crystal network. From this we conclude that such structures may have significant potential not in the conventional market place for porous structures, such as catalysis and ceramics but in the equally important arena of formulated products where the crystal network would impose overall structural properties with the release of active components such as agrochemicals, pharmaceuticals or cosmetics, controlled by its porosity, wall thickness and encapsulation properties.

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