In situ Brewster angle microscopy and surface pressure studies on the interfacial growth of mesostructured silica thin films

Karen J. Edler,*[a] Steve J. Roser*[a] and Stephen Mann[b]

[a] *Department of Chemistry, University of Bath, UK BA2 7AY. E-mail: K.Edler@bath.ac.uk; S.J.Roser@bath.ac.uk*
[b] *School of Chemistry, University of Bristol, Bristol, UK BS8 1TS. E-mail: S.Mann@bristol.ac.uk*

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Growth of a mesostructured silica thin film at the air/water interface was observed *in situ* using Brewster angle microscopy and surface pressure measurements allowing real time observation of nucleation of the film and its rapid growth to full surface coverage at the end of the induction period.

Mesoporous inorganic materials, such as the hexagonally ordered silica MCM-41, can be synthesized by template-directed reactions using surfactant or block copolymer self-assembled templates. Although much work has been carried out on the preparation of these materials in bulk, powdered forms, many applications particularly in the fields of filtration, separation and catalysis, require thin film geometries. Several groups have reported films formed by dip[1,2] or spin coating,[3] or by growth at the air/water,[4,5] mica/water,[6] and graphite/water interfaces.[7] Although films have been studied by X-ray and neutron reflectivity,[8–10] TEM and SEM,[11] AFM and optical microscopy,[12,13] none of these techniques have allowed detailed examination of the *in situ* growth of the silicate film. Here, we report the use of Brewster angle microscopy (BAM) and surface pressure measurements to trace the real-time evolution of growing films of mesostructured silica at the air/water interface. The data provide new insights into the formation mechanism and growth kinetics of such films as the measurements can be made on a much finer timescale than was previously possible. From these measurements it seems that the film is nucleated at many points across the surface and grows together from nuclei that are only a few microns across.

The growth of mesostructured silica thin films at the air/water interface of a synthesis solution† in a Langmuir trough showed three distinct stages observable by BAM: an induction period; a period of rapid film growth to cover the interface; and a period of coarsening of the surface film. The induction period (*ca.* 330 min from mixing), was characterized by a relatively constant value in the surface pressure measurements‡ (Fig. 1). The length of this period decreased with higher concentrations of CTAB and TMOS but was reproducible to within 10 min for a given set of conditions. A reproducible fluctuation in the surface pressure was observed during the induction period that consisted of a pressure increase followed by a decrease of *ca.* 1 mN m^{-1} between 125 and 285 min after mixing (Fig. 1).

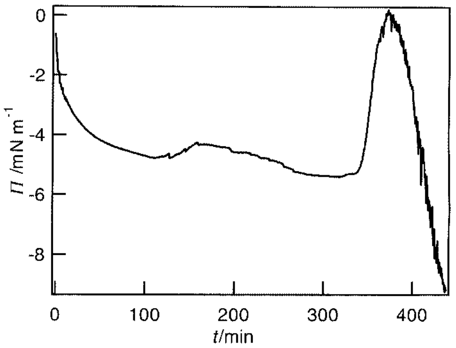

Fig. 1 Surface pressure changes with time during growth of a surfactant–silica mesostructured film at the air/water interface.

Corresponding BAM images§ taken during the induction period showed a uniform background with randomly distributed high-contrast point features, 5–10 μm in size [Fig. 2(a)]. These features increased slightly in number with time and moved across the interface owing to convection currents in the sub-phase. On the surface of a similar solution, CTAB in 0.2 M HCl with no TMOS present, such features are visible but are much less numerous and do not increase in number with time. Degassing the acid solution prior to adding CTAB and TMOS did not affect the appearance of the point features, indicating that they were not gas bubbles.

Taken together, the surface pressure measurements and BAM images indicate significant changes in the surface behaviour of the synthesis solutions prior to film formation. The results suggest that surfactant molecules are partitioned at the air/water boundary as a surface excess in the form of a continuous monolayer. Polysilicate binding to the cationic headgroups of the surfactant then gives rise to domains with modified thickness or molecular orientation. This is consistent with a model in which silicate binding in discrete regions under the monolayer is responsible for preferential nucleation of the silica–surfactant mesophase at the air/water interface, rather than bulk deposition in solution, although some precipitation from the bulk also occurs. An interaction between silica and surfactant at the surface of a CTAB/tetraethoxysilane solution has been proposed on the basis of X-ray and neutron reflectometry measurements.[4,9] These showed a slight decrease in the thickness of the surfactant monolayer from 3 to 2.7 nm and an increased scattering length density prior to film growth, indicating silica gathering at the interface. Reflectometry measurements, however cannot distinguish a low density, uniform silica/surfactant film from local regions of higher

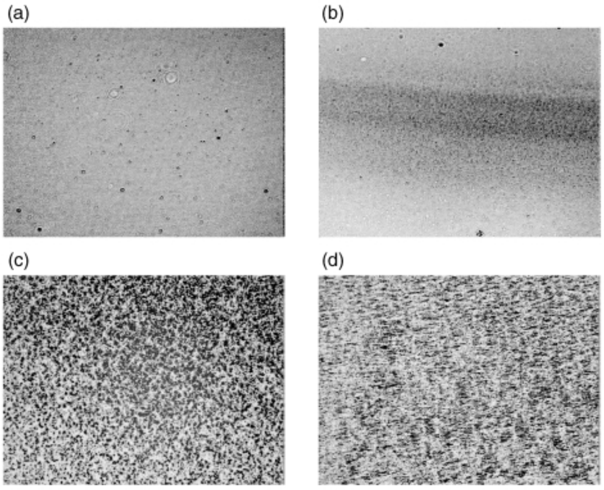

Fig. 2 Brewster angle microscope images following the evolution of a silica–surfactant composite film at the air/water interface (a) during the induction period, (b) just after the onset of film growth, 331 min after mixing of the reagents, (c) 350 min after mixing and (d) 407 min after mixing, showing growth and coarsening of the film at the interface. The horizontal edge of each image corresponds to 430 microns.

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density silica at nucleation sites scattered over the surfactant monolayer as is observed in the BAM.

The end of the induction period (330 min after mixing) was marked by a rapid increase in surface pressure over a period of 50 min (Fig. 1) owing to the formation of a densely packed surface film of mesostructured silica. Further growth resulted in an apparent decrease in pressure owing to the attachment of the film to and consequent increase in weight of the Wilhelmy plate. Corresponding BAM images showed an increase in the homogeneity of the surface film just prior to the rapid increase in surface pressure. Many of the point features in the BAM images became less distinct and merged with the background to give a lower contrast continuous texture that was still mobile on the liquid surface. Some point features were still visible, but their movement became associated with that of the continuous phase. The onset of film formation was associated with an increased density of the low contrast texture and a cessation of individual motion of the points over the whole region [Fig. 2(b)]. The texture then coarsened and became more distinct with growing visual contrast between dark and light regions, producing a dense coverage of 5–10 μm dots over the surface which began to merge [see Fig. 2(c)]. The lighter coloured horizontal bands across the image [Fig. 2(b)] were seen in most film forming preparations, appearing just prior to visible film formation in the BAM. They move across the surface in the same manner as the point features, so are connected with the surface, rather than the sub-phase. They do not appear in CTAB-only solutions and may be related to formation of oriented domains of the porous mesostructure in the growing surface film. Further evolution of the film, over 75 min from its first appearance, produced a network of strands with none of the original dots or the horizontal bands visible [Fig. 2(d)]. Similar fibrous structures in the final film have been reported using laser scanning confocal microscopy.[5]

The existence of point features with distinct contrast from the surrounding surface early in the induction period suggests that the film development process occurs *via* nucleation at many discrete points on the surface, rather than as a gradual building up of more or less uniform structures over the whole surface. During the induction period gradual condensation of the hydrolysed TMOS molecules proceeds, resulting in silica polyanions which interact with the surfactant monolayer at the interface causing nucleation of domains 5–10 μm across. These point features observed from the beginning the induction period are however, large compared to the coherence length expected from peak width studies of bulk hexagonal phase surfactant templated materials (several hundred nanometers[14]). Encouraging the growth of such domains may be a route to increasing long range homogeneity in these films. Once favourable conditions are achieved, possibly through concentration of the reacting species after evaporation of methanol, or by optimisation of headgroup spacing for the surfactant template by charge interaction with the polysilicates, the film forming process accelerates and full surface coverage is reached in a few minutes. Further condensation of the silica in the local environment and continuing addition of material from the sub-phase have been suggested to cause such films[5] to warp and buckle and are probably the cause of the development of ridges and the fibrous texture ultimately observed here.

Overnight, the film developed to a thickness of *ca.* 0.1 mm and showed macroscopic wrinkling, presumably induced by the confined area of the trough and from microscopic stresses such as local shrinkage of the system during polymerisation. *In situ* X-ray reflectometry on the final film showed two well developed broad Bragg peaks at $Q = 0.132$ and 0.257 Å^{-1} indicating formation of an ordered silica–surfactant mesophase. Reflectometry measurements however were too slow to follow the growth of the film during the induction period. Further work on the structural characterization of this material is in progress.

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Notes and references

† Thin films of mesostructured silica were prepared using a molar ratio of CTAB : water : HCl : TMOS of 1.53×10^{-3} :1:3.63×10^{-3}:0.011. The surfactant template, cetyltrimethylammonium bromide (CTAB, Sigma 99%) was dissolved in 0.2 M HCl and tetramethoxysilane (TMOS, Merck 98%) was added dropwise. This clear solution was transferred to a Teflon Langmuir trough 3.5 mm deep, surface area *ca.* 40 cm^2, so that the liquid formed a raised meniscus. Other experiments on this system have shown that at these reactant concentrations, films will grow in sealed containers where no evaporation can occur, however during these experiments, evaporation did occur and this undoubtedly affects film growth. Film formation was nevertheless highly reproducible with respect to induction time, morphology and surface pressure behaviour.

‡ Surface pressure measurements were made at 30 s intervals by a Wilhelmy plate method using a Nima surface pressure sensor. The measurements began 7 min after mixing, during which time the solution was poured into the trough and initial wetting of the Wilhelmy plate occurred. Evaporation of methanol generated by TMOS hydrolysis led to a change in plate buoyancy and an initial decrease in surface pressure; however this leveled off *ca.* 100 min after mixing. A similar although less rapid decrease in surface pressure of 0.7 mN m^{-1} owing to evaporation of water from the sub-phase was noted for a solution of CTAB in 0.2 M HCl with the same surface area in the absence of TMOS, over a 90 min period.

§ The Langmuir trough was mounted under a Brewster angle microscope (BAM2, Nanofilm Technologie GmbH) so that the surface structure and surface pressure of the synthesis solution could be monitored simultaneously. Light from a diode pumped frequency doubled Nd : YAG laser at 532 nm was used. At the Brewster angle, the reflectivity of polarised light at the interface is zero, so any small changes in interfacial refractive index, such as the presence of a surface film, are clearly visible. BAM images were taken every 30 s during the rapid growth phase of the film and every 5–10 min during the induction period. Evolution of the film structure was monitored in real time with the aid of a video camera attached to the BAM.

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