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Free-standing and oriented mesoporous silica films grown at the air–water interface

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SURFACTANT assemblies can function as templates for the deposition of silicates to form mesoporous silicas¹. Recently we described a surfactant-templated synthesis of oriented mesoporous silica films grown at the mica–water interface². Here we show that such films can be grown without a solid substrate, by surfactant templating at the interface between air and water. The films are continuous and have a root-mean-square surface roughness of about 3 Å. They are resilient enough to withstand significant bending, and are sufficiently flexible to be transferred onto substrates of different shapes. We propose a model for film formation which ascribes a dual-templating role to the surfactant: we suggest that both a surfactant overstructure at the air–water interface and micellar aggregates in solution interact collectively with the soluble, polymerizable silicate building blocks. These films might find applications in catalysis, separation technology and biomedicine.

Synthetic methods that enable the fabrication of oriented films of mesostructured materials provide opportunities for detailed studies of their anisotropy and size-tunable properties. This knowledge can be usefully exploited for the development of new technologies that depend on the special properties of this class of materials. Periodic mesostructures that are of current interest include semiconductors³, metal clusters⁴, porous solids⁵, composites⁶, block-copolymers⁷, liquid crystals⁸ and patterned self-assembled monolayers⁹.

Although oriented mesoporous thin films might find many applications as selective inorganic membranes, those that we described recently grown at the interface between mica and water² suffer from several limitations. In particular, few substrates have an atomically smooth surface and can sustain their structural integrity under the corrosive conditions of a synthesis, while at the same time facilitating oriented film formation. We considered that this problem might be surmounted by dispensing with a solid substrate and growing the films instead under surfactant overstructures at the interface between air and water.

The synthesis of mesoporous silica films at the air–water interface under acidic conditions¹⁰ is achieved using the following reactant mole ratios: 100 H₂O : 7 HCl : 0.11 CTACl : 0.07–0.13 TEOS; where CTACl is the cationic surfactant CH₃(CH₂)₁₅N(CH₃)₃Cl and TEOS is the silica source reagent (C₂H₅O)₄Si. The surfactant solution is mixed with TEOS and stirred for 2–3 minutes at room temperature and transferred into a polypropylene bottle. The film-forming process works well under static conditions at 80 °C over a reaction time of minutes to days. Well formed films, with thicknesses from tens of nanometres up to about half a micrometre have been grown at the air–liquid interface.

Scanning electron microscopy (SEM) images of the films that have been transferred onto a copper grid reveal that they are continuous, Fig. 1a. Polarized optical microscopy images (not shown) recorded at room temperature depict that the films are optically isotropic. This implies that the silica wall material is amorphous and that the micellar assembly contained within the channels is not behaving like a liquid crystal.

Transmission electron microscopy (TEM) images of microtomed sections cut orthogonally to the surface of the as-synthesized free-standing films show that the channels are hexagonally close-packed with a centre-to-centre distance of ~50 Å, Fig. 1b. This implies growth of the channels in an orientation parallel to the air–water interface. The observation of a smooth film surface grown at the air–water interface with a root-mean-square roughness of ~3 Å indicates that the growth process occurs via deposition of silica-surfactant micellar solution precursors at a surfactant overstructure localized at this interface. The film surface growing into the solution shows roughness on the mesoscopic scale, which might represent a silica replica of the disposition of micellar structures as they are deposited at this lower surface (Fig. 1c).

Early-stage free-standing films, lifted onto TEM grids and viewed directly, are sufficiently thin to be imaged at an accelerating voltage of 50 kV (Fig. 1d). Under these conditions, a highly ordered periodic structure with a spacing of ~25 Å is observed. The observed 25 Å periodicity is consistent with a hexagonal close-packed arrangement of one-dimensional channels viewed orthogonally to the film surface¹¹. The image is consistent with the proposal that the channels are oriented parallel to the surface of the film. TEM images (not shown) of calcined (450 °C for 4 h in air) free-standing films demonstrate that the mesopore order is intact.

SEM images show that the films are resilient to bending (Fig. 1e). They have been transferred onto substrates with different shapes. These properties may reflect the thin organic–inorganic composite nature of the films. Together with complementary powder X-ray diffraction studies, the results demonstrate that the macroscopic integrity and the mesopore order of the attached films are intact.

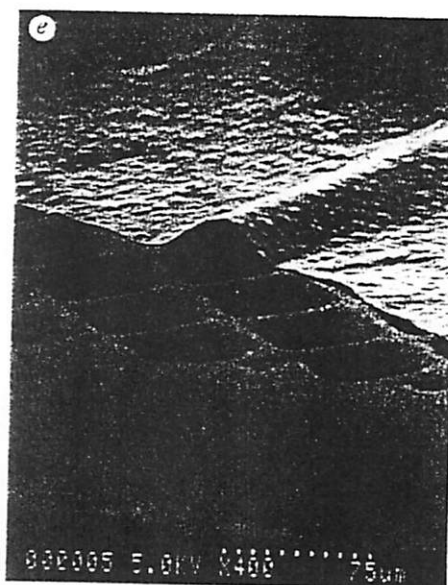
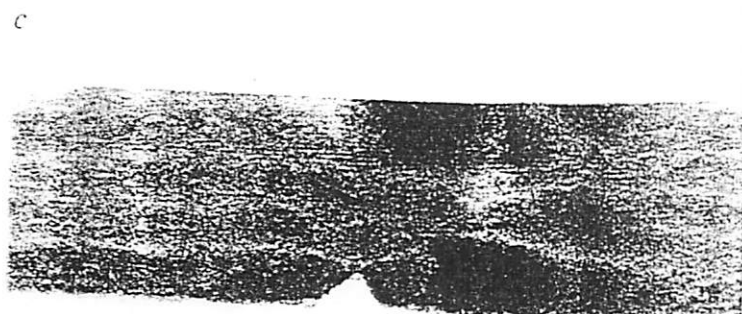
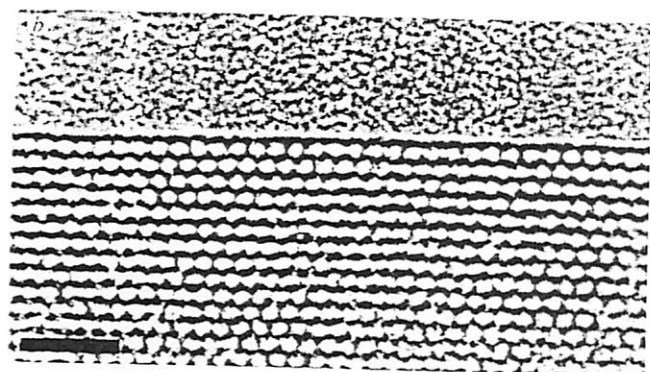
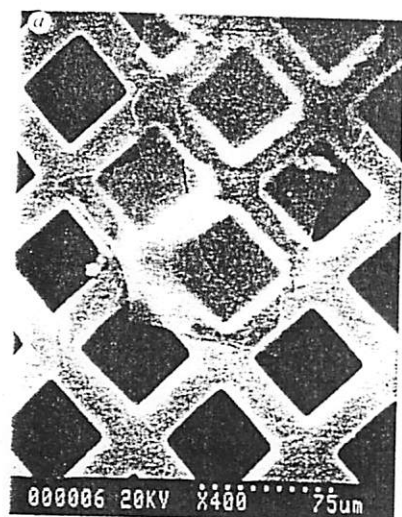


FIG. 1 a, SEM image (recorded on a Hitachi S-570 microscope at an accelerating voltage of 20 kV) of a free-standing film that has been transferred from the air-water interface onto a copper grid. The film is continuous, and is transparent under the imaging conditions. Dotted scale bar, 75 μm . b, TEM image (obtained on a Philips 430 microscope operating at 100 kV, epoxy-embedded and microtomed 100–300 Å sections cut orthogonally to the film surface) of an as-synthesized free-standing film. The film surface shown is the one formed at the air-water interface, where the channels are seen to run parallel to this interface. Scale bar, 25 nm. c, TEM image of an as-synthesized free-standing film (prepared for imaging as in b) showing the difference between the surface roughness at the top of the film (which grows at the air-water interface) and the bottom (which grows into the solution). Scale bar at the bottom, 250 nm. d, TEM image of a free-standing film (viewed normal to the air-water interface) showing a highly ordered periodic structure consistent with a hexagonal close-packed arrangement of channels running parallel to the surface of the film. Scale bar, 25 nm. e, SEM image of a free-standing mesoporous silica film which has been transferred from the air-water interface onto a copper grid. The film shows extensive regions of film curvature. Dotted scale bar, 75 μm .

Atomic force microscopy (AFM) is an effective probe of the overall topological landscape and structural detail of the surface of the mesoporous silica films (Fig. 2). AFM scans over large areas of the film provide an estimate of the root-mean-square roughness of the surface grown at the air-water interface to be ~ 2 Å which is in good agreement with the TEM results (Fig. 1). AFM images of the films reveal parallel surface features with a periodicity of ~ 50 Å which appear to have a spheroidal texture. This is consistent with the TEM observations of the internal channel architecture of the films. The main features in these AFM images were reproducible with respect to different scans, scan directions, load forces, tips and samples, and are not considered to portray imaging artefacts. Some of the irregularities observed in the surface of the film could arise from inhomogeneous silicate condensation processes. Overall, the observed surface topology may be viewed as a silica replica of the distribution of head groups

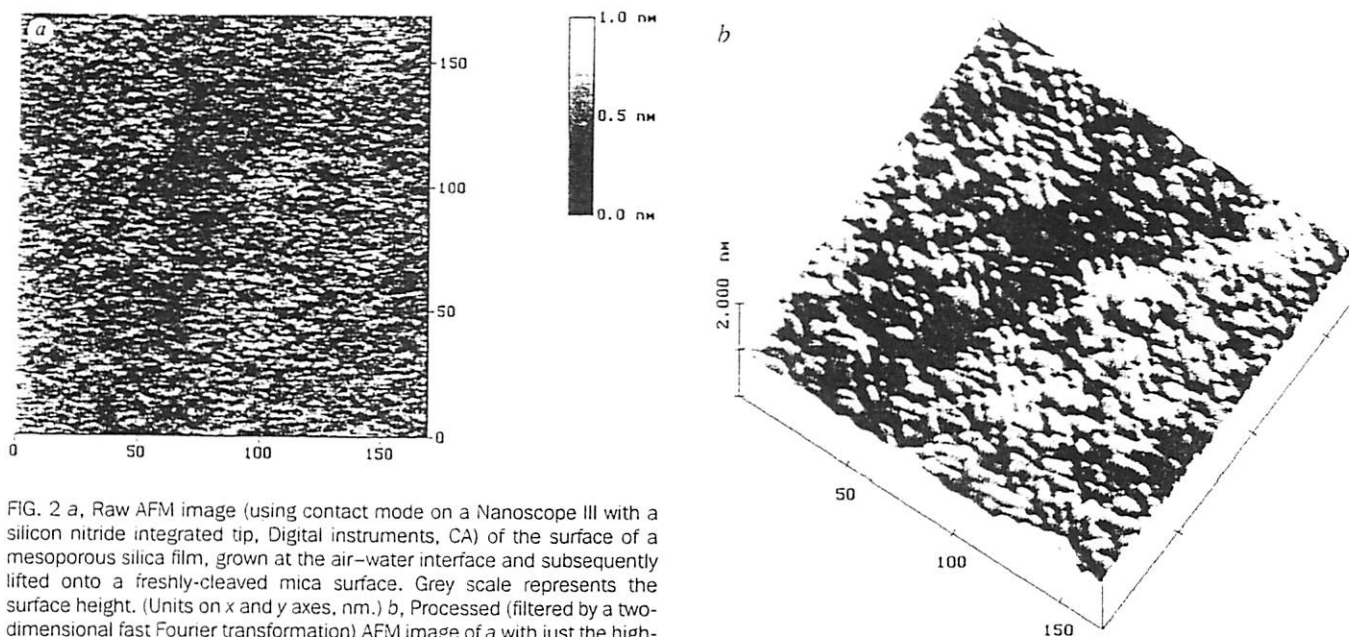


FIG. 2 a, Raw AFM image (using contact mode on a Nanoscope III with a silicon nitride integrated tip, Digital Instruments, CA) of the surface of a mesoporous silica film, grown at the air–water interface and subsequently lifted onto a freshly-cleaved mica surface. Grey scale represents the surface height. (Units on x and y axes, nm.) b, Processed (filtered by a two-dimensional fast Fourier transformation) AFM image of a with just the high-frequency noise removed, revealing parallel surface features with a periodicity of 50 Å and a spheroidal texture. (Units on x axis, nm).

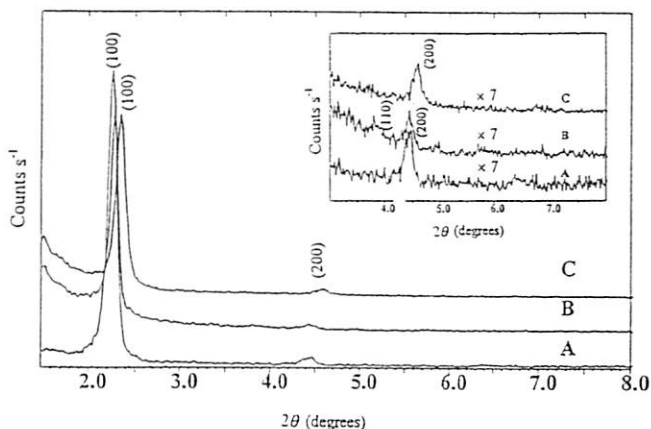


FIG. 3 Powder X-ray diffraction patterns (recorded on a Siemens D5000 diffractometer, using Ni-filtered Cu K α radiation with wavelength $\lambda = 1.54178$ Å). Traces A and C, free-standing as-synthesized (A) and calcined (C) mesoporous silica films, showing (100) and (200) reflections. Trace B, powdered samples obtained by removing the as-synthesized films from the substrate, showing the expected (100, 110, 200) reflections. The absence of the (110) reflection for the film samples confirms that the channel axis is oriented parallel to the templating liquid surface. Inset, PXRD reflections for $2\theta = 3^\circ$ – 8° with an intensity (counts per second) scale expansion of $\times 7$.

of the surfactant overstructure and the micellar moieties existing at the interface between air and water.

The powder X-ray diffraction patterns for the as-synthesized and calcined free-standing films, lifted onto a solid substrate, are shown in Fig. 3. They both reveal (100) and (200) reflections consistent with the TEM observations that the channels run parallel to the surfactant overlayer at the air–water interface. By contrast, powdered samples obtained by removing these films from the substrate show the expected (100, 110, 200) reflections. The absence of the (110) reflection for the film samples confirms that the channel axis is oriented parallel to the templating liquid

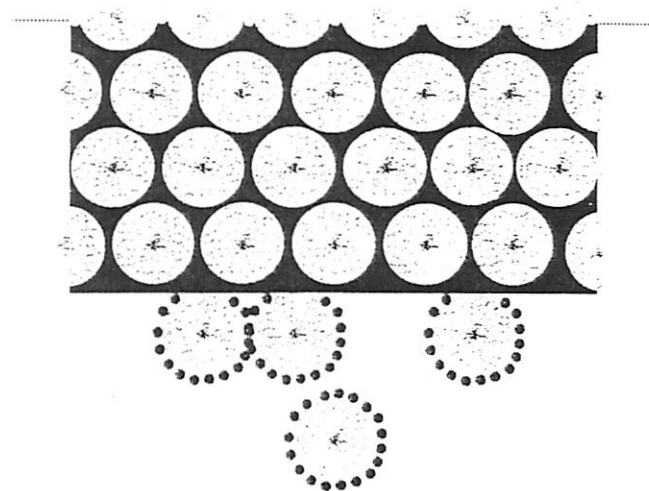


FIG. 4 Graphical illustration of the proposed model for the formation of a free-standing oriented mesoporous silica film at the air–water interface. This model involves a dual-templating role for the surfactant, and is based on collective interactions between polymerizable silicate building-blocks, a surfactant overstructure and solution micellar aggregates. Light grey, surfactant; grey, silicate building-block; black, silica. The air–water interface is represented by the dotted line at the top of the figure. The white background at the bottom of the figure represents bulk aqueous synthesis mixture.

surface, consistent with the TEM results. On calcination of the films, the anticipated contraction ($\Delta d_{100} = 2$ – 5 Å) of the hexagonal *ab*-unit cell is observed, due to the removal of the surfactant template from the channels, concomitant with the condensation of silanol (SiOH) groups in the channel walls^{1,2}.

A model for the growth of smooth and oriented mesoporous silica films at the air–water interface must take into account recent studies of mechanistic pathways for the formation of mesoporous silicas in the bulk powdered form¹² and the surface profile of soluble surfactant overlayers at the air–water interface^{13–16}. First, the general consensus is that mesoporous silicas

form through the co-assembly of surfactant-silicate micellar aggregates into a silicatropic mesophase which undergoes condensation-polymerization into a silica replica of the templating interfaces¹². Second, the arrangement of head groups for surfactants in water-soluble overlayers has recently been studied by X-ray and neutron reflectometry as well as equilibrium molecular dynamics simulation techniques¹³⁻¹⁶. In the case of CTACl, surfactant overlayers are in equilibrium with the underlying solution. Published results¹³⁻¹⁶ suggest that the surface profile has a surfactant 'hemi-micellar' wave-like structure rather than a planar close-packed one as found for surfactants in insoluble monolayers. The surface roughness, as defined by the gaussian distribution of CTACl head groups, is $\sim 3-4$ Å.

We propose that the formation of a mesoporous silica film involves collective interactions between silicate building-blocks, micellar solution species and a surfactant 'hemi-micellar' overstructure localized at the air-water interface (Fig. 4). Under the synthesis conditions used, film formation is considered to involve polymerization of silicates in the surfactant head group regions of a hexagonal mesophase that is concentrated at the liquid surface overstructure. This is reasonable as hexagonal phases have been observed at the liquid surface of micellar solutions¹⁶. Thus a pre-organized CTACl overlayer facilitates the organization of a smooth oriented mesoporous silica film at the air-water interface. The observed root-mean-square roughness of the films reflects the outcome of a cooperative surface process in which silicates undergo a condensation-polymerization at a templating overstructure. Film growth is probably regulated by matching charge and geometry between micellar aggregates and silicates at a surfactant structured air-water interface.

The availability of free-standing and oriented mesoporous silica films provides opportunities for tailoring their structures, pore sizes and compositions, altering their adsorption properties, and chemically modifying their surface reactivity. These mesostructured films may find uses as organized catalysts, membranes for biomolecule separations, sensors for large molecules, ordered ceramic matrix composites, engineered biomaterials and mesostructured semiconductors. □

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