

## Peering Into the Self-Assembly of Surfactant Templated Thin-Film Silica Mesophases

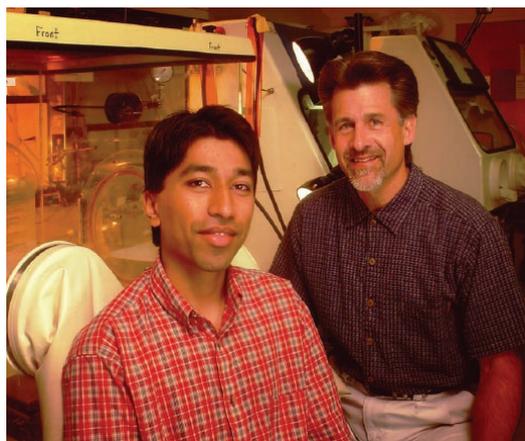
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*In this study, time-resolved grazing incidence small angle x-ray scattering (GISAXS) was combined with gravimetric analysis and infrared spectroscopy to structurally and compositionally characterize in situ the evaporation-induced self-assembly (EISA) of a homogeneous silicasurfactant/solvent solution into a highly ordered surfactant-templated mesostructure. Using detergent-like molecules of cetyl trimethyl ammonium bromide (CTAB) as the structure-directing agents, a two-dimensional hexagonal thin film with cylinder axes oriented parallel to the substrate surface forms from an incipient lamellar (layered) mesophase through a correlated micellar intermediate. A comparison with the corresponding CTAB/water/alcohol system (prepared without silica) shows that the hydrophilic and non-volatile silicic acid components actively participate in self-assembly and, along with the presence of solid-liquid and liquid-vapor interfaces, significantly influence the self-assembly pathway.*

It is now recognized that self-assembly is a powerful synthetic approach to the fabrication of nanostructures with feature sizes smaller than achievable with state-of-the-art lithography, and with a complexity approaching that of biological systems. For example, recent research has shown that silica/surfactant self-assembly can direct the formation of porous and composite thin film mesostructures characterized by precise periodic arrangements of inorganic and organic constituents on the scale of one to 50 nanometers in size. Despite the potential utility of these films for a diverse range of applications, such as sensors, membranes, catalysts, waveguides, lasers, nano-fluidic systems, and low dielectric constant insulators, the mechanism of thin film self-assembly remains largely unexplored. Understanding and ultimately controlling self-assembly is critical in order for it to transition from largely a laboratory practice to a reliable 'tool' for nanofabrication.

In this study we used time-resolved GISAXS combined with gravimetric analysis to structurally and compositionally characterize *in situ* the EISA process. Solutions were dispensed onto a silicon substrate positioned horizontally on the platform of a weighing balance that was confined within a cell, allowing controlled solvent evaporation. The liquid spectrometer at beamline X22B allowed the x-rays to impinge upon the surface at grazing incidence, and the scattering was continuously collected onto a charge-coupled device camera. *In situ* stress and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) measurements, performed using



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### BEAMLINES X22B, X22A

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the identical horizontal geometry and x-ray reflectivity analysis of the final self-assembled films, enabled further structural interpretation of the GISAXS results, providing greater insight into the self-assembly pathway.

**Figure 1** shows the temporal evolution of starting weight percentage for the 0.12 sample (where 0.12 is the CTAB-to-Si molar ratio), along with that calculated for the surfactant, CTAB. The self-assembly pathway comprises four successive stages: (I) isotropic, (II) lamellar, (III) correlated micellar, and (IV) hexagonal, where each is characterized quantitatively by the  $d$ -spacing observed normal to the substrate, and, for the hexagonal phase, the in-plane spacing  $a_{\text{fcr}}$  (where fcr is the face-centered rectangular lattice representation of the hexagonal lattice). **Figure 2** maps the evaporation-induced compositional trajectories of the three CTAB/silica systems onto the bulk water/ethanol/CTAB phase diagram. Also plotted is the trajectory for the sample prepared without silica (WS). Selected corresponding GISAXS patterns obtained after the specified times,  $t$  (seconds), are presented.

The formation of the lamellar phase (Region II in **Figure 1**, inset **b** in **Figure 2**) is completely unexpected from the bulk phase diagram and is not observed in the WS system. Based on orientation, we attribute its appearance to the local enrichment of the sol (the silica/surfactant/solvent solution) at the liquid-vapor interface. We also observe a continuous reorganization of both the mesostructure and the lattice dimension within Regions II-IV (**Figure 1**) that results from the reorganization of the surfactant molecules within the lamellar or micellar structures due to ethanol evaporation. For all samples of CTAB and the other surfactant systems that were studied, we find that the presence or absence of hydrophilic silica species dramatically influences mesophase development. Generally, without silica, the evaporation of solutions like WS results in a crystalline surfactant product without forming the mesophase(s) anticipated from the bulk phase diagram. This apparent kinetic effect presumably results from the evaporation of water. We suppose that such kinetic barriers are avoided for silica-containing systems because the silicic acid species serve as non-volatile fluids that are as hydrophilic as water.

As a result of this study, we now recognize the opportunity to controllably interrupt EISA to derive novel intermediate sandwich-like structures or fine-tune the  $d$ -spacing and its associated properties, such as surface area, refractive index, and dielectric constant.

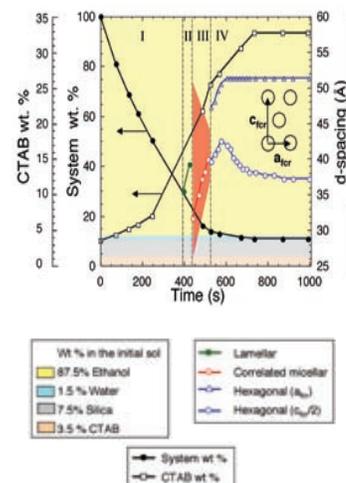
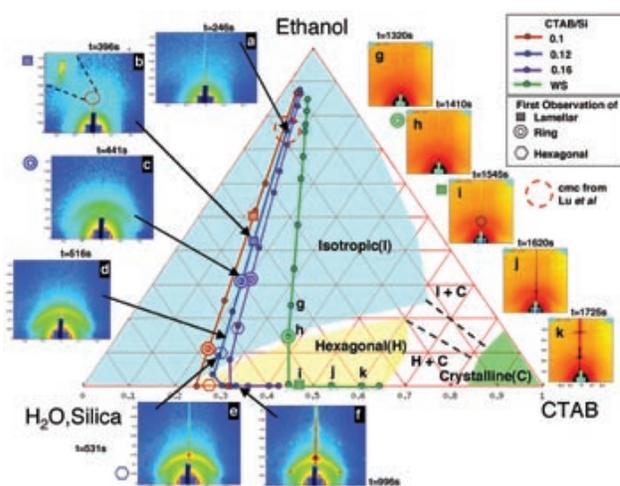


Figure 1. The temporal evolution of structure and composition for the 0.12 sample.

Figure 2. Bulk and thin-film ternary phase diagram. The evaporation-induced compositional trajectories of the three CTAB/silica systems (0.10, 0.12, and 0.16) and the WS systems are mapped onto the bulk water/ethanol/CTAB phase diagram, considering the hydrophilic silicic acid precursors to be equivalent to water. For the 0.12 sample (a) corresponds to the isotropic phase, (b) the lamellar, (c & d) the correlated micellar, and (e & f) the hexagonal. For the WS sample, (g) corresponds to isotropic, (h) correlated micellar, (i & j) lamellar and correlated micellar, and (k) to crystalline CTAB.