ESRF	**Experiment title:** **Formation of Non-ionic Surfactant Templated Titania Mesostructured Films at the Air-Water Interface**	**Experiment number**: CH-1914
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Report:

The aim of this experiment was to continue our recent work on the formation mechanisms of mesostructured surfactant-templated inorganic thin films that grow at the air-water interface.[1-3] We have recently extended our work in this area to titania-surfactant thin films. These films grow at the air-solution interface from dilute solutions containing a titania precursor and the appropriate surfactant species.[4] Free-standing mesostructured titania films have potentially important applications not only as membranes but also for photocatalysis, in semiconducting layers and photochromic devices. Our preliminary experiment on titania films focused on the structural effects of altering the concentration of an anionic surfactant template, sodium dodecylsulphate (SDS), and the acid concentration of the synthesis solutions. In this experiment we investigated the film development process and structures formed when using a non-ionic surfactant template, which has a poly(ethylene oxide) headgroup. Non-ionic surfactants are generally cheaper and more susceptible, in the long term, to biodegredation making them more environmentally friendly than anionic surfactant species. In silica films a larger range of mesostructures are accessible using nonionic surfacants than are found using charged surfactants. Our previous experiment showed that the mesostructure in the titania films was highly dependent upon the acid concentration for films templated with an anionic surfactant, so in this experiment we studied changes in both the acid concentration, and the concentration of the titania precursor for a constant surfactant template concentration.

Films were prepared using titanium (IV) tetrabutoxide (TBOT) as the titania precursor, and the nonionic surfactants Brij56 (~$C_{16}H_{33}EO_{20}$) and Brij76 (~$C_{18}H_{37}EO_{20}$) in acidic solutions. The acid concentration was varied between 0.7M and 1.4M. For these experiments the molar ratio was: TBOT / HCl / water / surfactant : 1.7×10^{-3}/ X / 1/ 2.8×10^{-4}, where X varied between 0.014 to 0.029. For experiments where the TBOT concentration was varied the molar ratio was: TBOT / HCl / water / surfactant : X / 0.029/ 1/ 2.8×10^{-4}, where X varied between 2.6×10^{-3} and 8.5×10^{-4}. Solutions were prepared by initially mixing the titania precursor and acid in one solution, and the surfactant and water separately. The two solutions

were then added together and poured into a teflon trough for the reflectivity measurements.

Films prepared using the shorter chain Brij56 surfactant developed over a few hours at the air-solution interface, allowing time-resolved measurements to be made on these solutions. Films grown from the longer chain surfactant Brij76 however showed a well-developed diffraction peak in the off-specular scattering as soon as the sample alignment process was finished, indicating film growth was occuring in less than 4 minutes in these systems. Specular reflectivity measurements and grazing incidence diffraction measurements were made on the films once growth appeared to cease. Surprisingly, although all solutions showed peak development in the time-resolved off-specular scattering measurements, with relatively sharp peaks appearing close to the specular reflection peak, little structure was found in the final films. Specular reflectivity patterns showed a series of broad bumps in the best cases, and smooth fall-off in the worst. Grazing incidence diffraction patterns showed several strong peaks close to δ=0 which formed short arcs around this position, but no higher order peaks were observed at larger angles. The peak spacings however do not correspond to a lamellar phase. No precipitate was formed in the bulk of the solution in these solutions so ordering can only have been present in the interfacial films, which were clearly visible to the eye at the surface of the solutions. Further measurements on dried films harvested from the solution surface will be made to help determine the nature of the mesoscale structure. It is possible that these surfactants, which have some polydispersity in the headgroup, produce films with a lower degree of long range order so that only one order of diffraction is present. This would correspond to the case observed for bulk templated material produced using these surfactants,[5] although, in the case of thin films as we saw previously for silica, the influence of the interface usually promotes a higher degree of ordering than is seen in the bulk.

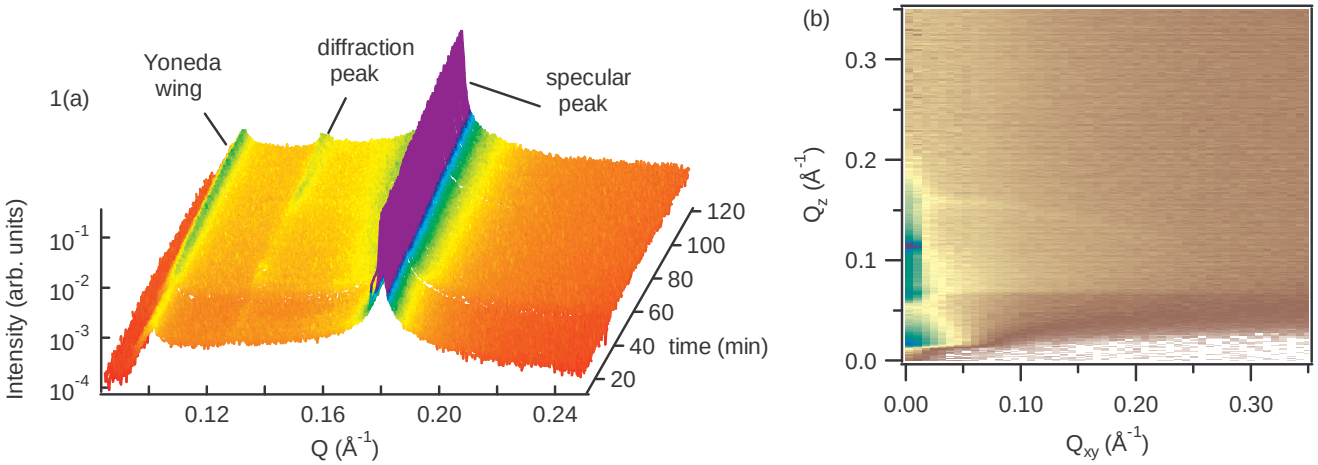

Figure 1(a) off-specular time resolved data for a film grown at TBOT / HCl / water / surfactant : 1.7×10^{-3}/ 0.014 / 1/ 2.8×10^{-4} showing development of the diffraction peak indicating mesostructural order at the interface. (b) grazing incidence diffraction from the same film.

References

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