X-Ray reflection studies on the monolayer-mediated growth of mesostructured MCM-41 silica at the air/water interface

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X-Ray reflection has been used to study the nucleation and growth of thin films of a silica–surfactant mesophase (MCM-41) at the air/water interface in the presence and absence of an insoluble lipid monolayer of phosphatidylcholine; the rate of self-assembly and structural order of films comprising up to four micellar layers were enhanced under the lipid monolayer.

One of the most promising routes to new silica-based mesostructured materials with pore diameters greater than those of conventional materials such as zeolites involves the co-operative assembly of inorganic precursors with supramolecular organic templates.[1–7] The resulting silica–surfactant liquid crystalline mesophases can have a range of symmetries, including hexagonal (MCM-41) or cubic (MCM-48), and can be processed to produce mesoporous replicas consisting of an ordered array of channels with 1 nm thick silica walls. Several studies have recently shown that thin films of MCM-41 materials can be formed under acidic conditions at the air/water,[8] mica/water,[9] or graphite/water interface,[10] as well as on Au substrates that had been chemically patterned.[11] In a recent study,[12] X-ray reflection (XRR) was used to investigate the time-dependent growth of MCM-41 under acidic conditions at the air/water interface. In this report we use X-ray reflectivity to probe the nucleation and growth of thin films of MCM-41 under alkaline conditions at the air/water interface in the presence of an insoluble lipid monolayer that acts as a secondary template in the self-assembly process.

MCM-41 silica was synthesised at room temperature from a dilute basic solution *via* condensation of tetraethoxysilane (TEOS) in the presence of hexadecyltrimethylammonium bromide (C_{16}TMABr).‡ The films were grown slowly at the air/water interface from a quiescent solution contained within a Teflon trough which was sealed in a Perspex box with thin Mylar windows for X-ray transmission. In experiments involving phosphatidylcholine (PC) monolayers, a known volume of PC in chloroform was spread onto the air/water interface prior to recording of the XRR data.§ Analysis of X-ray reflection data was performed according to established procedures.¶

Fig. 1 shows the fitted reflectivity profile and calculated scattering density (inset) for the initial measurements for MCM-41 films grown from alkaline solutions under a PC monolayer. The zero-time fit has a fringe periodicity which corresponds to a thickness of 4 nm and demonstrates that the electron density profile perpendicular to the surface has two maxima, both of which have similar electron density values. The presence of the fringes indicates that a single micellar layer of a silicate–surfactant film is nucleated under the lipid monolayer. Similar data were obtained for the zero-time measurements for MCM-41 grown at an unmodified air/water interface, except that the peak values of the scattering length density profiles were slightly lower, suggesting that the presence of the PC monolayer induced the nucleation of a more densely packed arrangement of silicated rod-like micelles. In both cases, the model used to fit the data was based on a layer of amorphous silica-coated cylindrical micelles with an overall diameter of 4 nm. Interestingly, the data could not be fitted with a model corresponding to a primary surface layer of hemispherical micelles, as has been recently proposed as the initial stage in the nucleation of MCM-41 films from acidic solutions.[8] Thus, under alkaline conditions, mineralized micellar cylinders are considered to constitute the first layer of MCM-41 nuclei formed at the air/water or monolayer/solution interfaces.

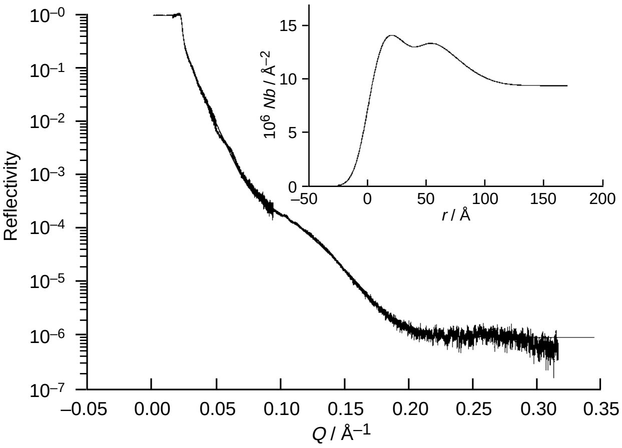

Fig. 1 Fitted reflectivity profile and calculated scattering length density (*Nb*, inset) for MCM-41 films grown for 1 h under a PC monolayer

Significant differences were observed in the XRR scattering length density profiles for thin films grown for 3 days under a PC monolayer (Fig. 2). The complex profile shows five distinct peaks with a repeat spacing of 3.9 nm in the density plot, leading to a broad Bragg peak centred at ***Q*** *ca.* 0.16 Å^{-1}. If the cylinders are hexagonally close packed, this corresponds to a film consisting of four silica–surfactant micellar layers, but with the scattering length density less than that expected from a perfectly ordered structure. The Bragg peak was consistent with small angle powder XRD and electron diffraction data of the retrieved thin films which confirmed the formation of the hexagonal mesophase.‖ In contrast, the MCM-41 silica prepared at the unmodified air/water interface showed a less well developed

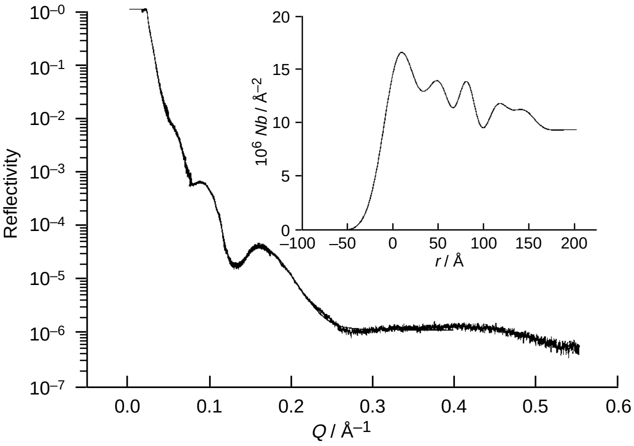

Fig. 2 Fitted reflectivity profile and calculated scattering density (inset) for MCM-41 films grown for 3 days under a PC monolayer

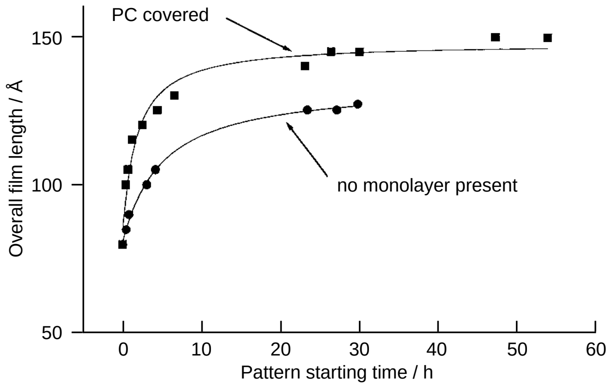

Fig. 3 Plot of film thickness *vs*. time for MCM-41 deposition from monolayer-covered and uncovered reaction solutions

fringe structure, and no Bragg peak after 48 h (data not shown). This indicates that under these conditions the silica–surfactant mesophase was significantly less ordered perpendicular to the air/water interface than the thin film nucleated under the lipid monolayer.

We also undertook preliminary studies on the time-dependence of the Bragg peak and scattering length profiles. In the presence of the PC monolayer, a Bragg peak at 0.16 Å^{-1} was discernible after 4 h and clearly visible after 1 day. After this time, the peak did not change in position, width or intensity, indicating that the ordered internal structure was stable at the monolayer/solution interface. The scattering length profiles were used to determine the rate of growth in thickness of the MCM-41 films and clearly indicated that the presence of the PC monolayer results in faster growth and a more ordered mesophase (Fig. 3).

In conclusion, we have demonstrated that it is possible to obtain detailed information on the growth and structure of mesostructured MCM-41 silica films at the air/water interface using X-ray reflection. Spreading of a PC monolayer at the air/water interface enhances the rate of formation and quality of the thin films, suggesting that interactions between the lipid headgroups and molecular or supramolecular silica/surfactant species facilitate the assembly of the first layer of the nucleus. Further work using a range of lipids and their associated phase behaviour is underway to elucidate these interfacial processes.

Notes and References

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‡ In a typical experiment, 0.16 g of C$_{16}$TMABr was dissolved in 318.0 g of H$_2$O and stirred continuously. 2.0 g of 1 M NaOH were added, followed by 0.828 cm^3 of TEOS, (molar composition = 0.001 C$_{16}$TMABr : 0.11 NaOH : 0.009 TEOS : 40.2 H$_2$O). The solution was left to stir for 3 min before being placed in the Teflon trough of the X-ray reflectometer. Growth of the MCM-41 film was extremely slow because of the constant vapour pressure of ethanol in the sealed environment which arose from the initial condensation reactions. In contrast, the results of ref. 12 were obtained from an evaporative environment. Measurements were made using an in-house energy-dispersive X-ray reflectometer, and typically consisted of three separate runs at different angles, lasting in total for 1 h. Measurements of MCM-41 growth were taken over a period of several days.

§ 124 μl of a chloroform solution of PC (100 mg cm^{-3}) were spread at the air/water interface using a micro-syringe. The volume added was calculated to produce a solid phase monolayer after solvent evaporation.

¶ In general, each discontinuity in scattering length density (Nb/Å^{-2}) between thin layers lying parallel to the interface under investigation contributes to the X-ray reflectivity, given by the well known Fresnel coefficient. This is modified by a factor, which allows for the roughness of the interface. The contributions from each layer are then combined using a matrix method. The usual procedure in fitting a reflectivity profile is to assume a model profile, and allow variation of numerous parameters, until the best fit between the model and the real $R(\boldsymbol{Q})$ is found. The layer electron density in Å^{-3} can be determined by dividing Nb by the scattering length of a single electron (2.8 × 10^{-5} Å). Thus, the experiment measures the change in electron density perpendicular to the air/water interface, but averages information in the plane of the surface. Further details can be found in ref. 13.

‖ Samples for SAXRD, electron diffraction, ^{13}C and ^{29}Si solid state NMR, FTIR and TGA were collected from the air/water or monolayer/water interfaces after growth for 3 days in an unsealed environment. Data for monolayer-mediated synthesis; SAXRD *d* spacings, 4.0, 2.31, 1.99, 1.51 nm (as-synthesized), 3.16, 1.97, 1.75 nm (calcined); ^{29}Si NMR, δ −89.7 (Q^2), −99.6 (Q^3), −109.4 (Q^4) (as-synthesized); ^{13}C NMR, δ 14.46, 23.25, 26.99, 30.68, 32.62, 54.04, 66.91 (as-synthesized); FTIR, ν(Si–O–Si) 1000–1200 cm^{-1}, ν(CH$_2$) 1460–1490, 2850–2950 cm^{-1}; CHN analysis, 32 mass% C (as-synthesized). Hexagonal arrays of 4 nm spaced lattice fringes were observed by TEM.

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonwicz, C. T. Kresge, K. D. Schmitt, C. T. Chu, D. H. Olsen, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.
3 A. Firouzi, D. Kumar, L. M. Bull, T.Besier, P. Sieger, Q. Hue, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky and B. F. Chemelka, *Science*, 1995, **267**, 1138.
4 Q. S. Huo, D. I. Marglose, U. Ciesla, D. G. Demuth, P. Y. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.
5 D. Khushalani, A. Kuperman, G. A. Ozin, K. Tanaka, J. Garces, M. M. Olken and N. Coombs, *Adv. Mater.*, 1995, **7**, 842.
6 J. H. Koegler, H. W. Zandbergen, J. L. N. Harleveld, M. S. Nieuwenhuizen, J. C. Jansen and H. Vanbekkum, *Stud. Surf. Sci. Catal.*, 1994, **84**, 307.
7 J. C. Jansen and G. M. Vandrosmalen, *J. Cryst. Growth*, 1994, **128**, 1150.
8 H. Yang, N. Coombs, I. Sokolov and G. A. Ozin, *Nature*, 1996, **381**, 589.
9 H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara and G. A. Ozin, *Nature*, 1996, **379**, 703; I. A. Aksay, M. Trau, S. Manne, I. Hunma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger and S. M. Gruner, *Science*, 1996, **273**, 892.
10 H. Yang, N. Coombs, I. Sokolov and G. A. Ozin, *J. Mater. Chem.*, 1997, **7**, 1285.
11 H. Yang, N. Coombs and G. A. Ozin, *Adv. Mater.*, 1997, **9**, 811.
12 A. S. Brown, S. A. Holt, Thien Dam, M. Trau and J. W. White, *Langmuir*, 1997, **13**, 6363.
13 J. Penfold and R. K. Thomas, *J. Phys: Condens. Matter.*, 1990, **2**, 1369.

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