

# Supporting Information: Film Before Aggregates: An *operando* GISAXS Study on Electrochemically Assisted Surfactant Assembly

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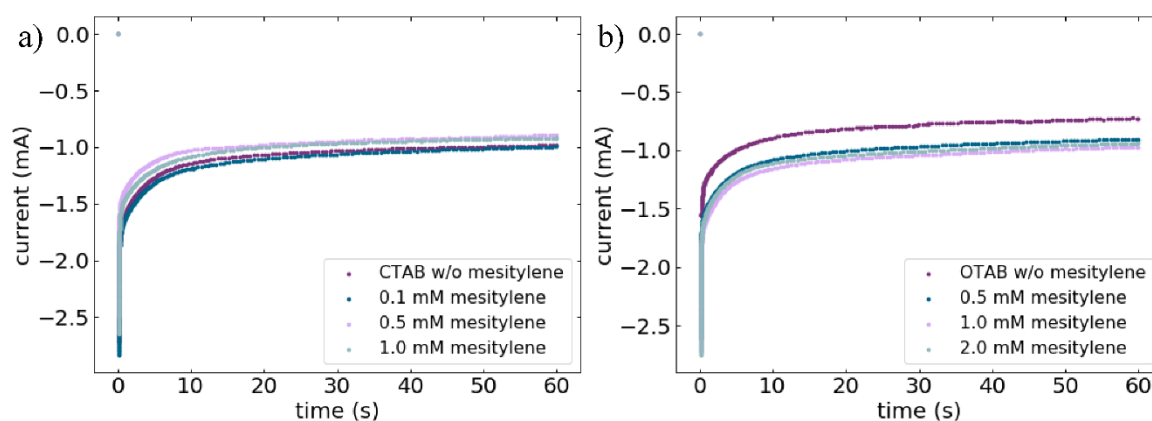


Figure S1: Chronoamperometry of silica films deposited using different solution compositions. The potential was stepped from open circuit to -2 V and then maintained for 60 s for all depositions using a) CTAB and b) OTAB as the surfactant.

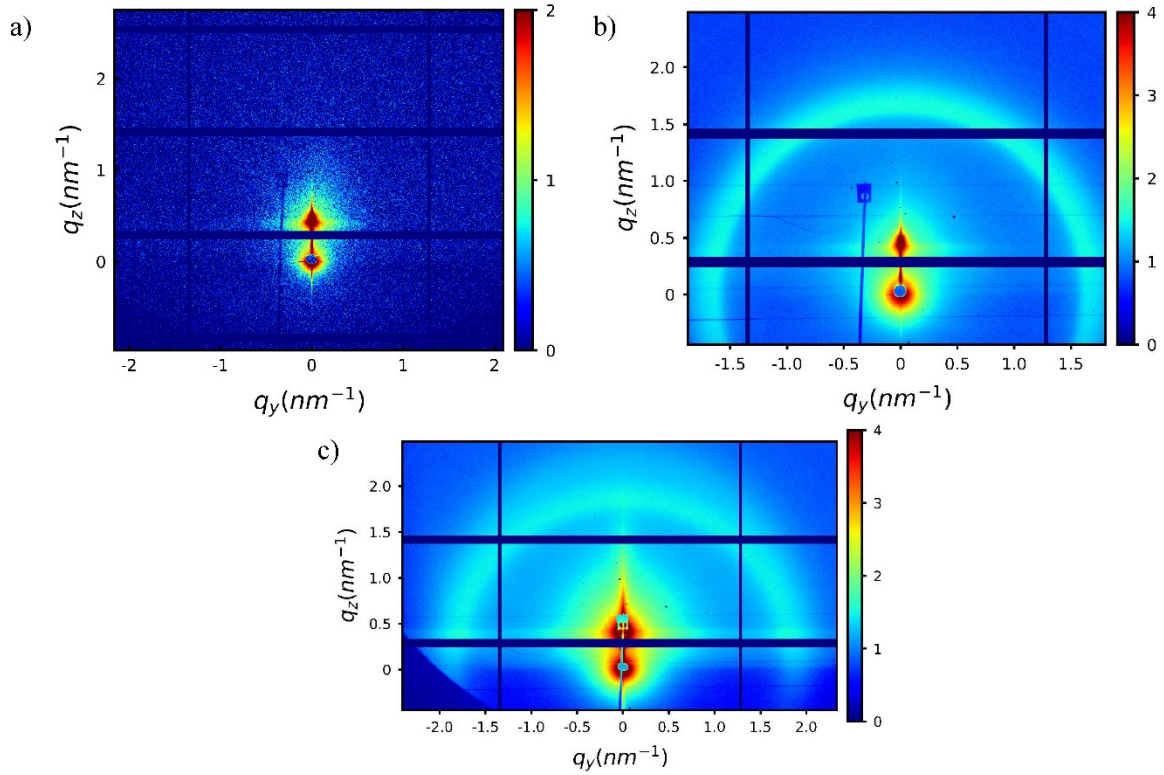


Figure S2: Scattering images for a) 0 s, b) after deposition and c) after ageing of the samples. Exposure times: 0.1 s, 5 s and 60 s respectively. Incident angle:  $0.2^\circ$ .

Table 1	First appearance	After deposition	After ageing
$q_y$ ( $\text{nm}^{-1}$ )	$1.66 \pm 0.16$	$1.63 \pm 0.16$	$1.78 \pm 0.24$
$d$ (nm)	$3.78 \pm 0.07$	$3.86 \pm 0.38$	$3.53 \pm 0.48$

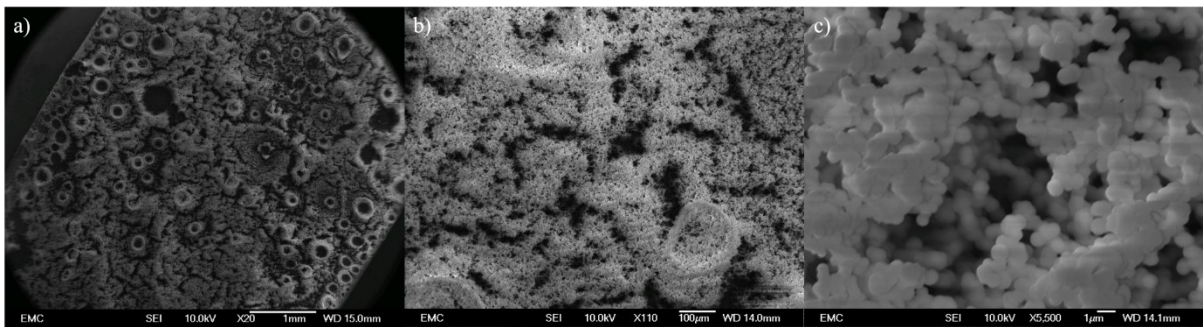


Figure S3: SEM images of sample A1 at magnifications of x20, x110 and x5500. 10 kV acceleration voltage was used. The sample was not coated prior to microscopy.

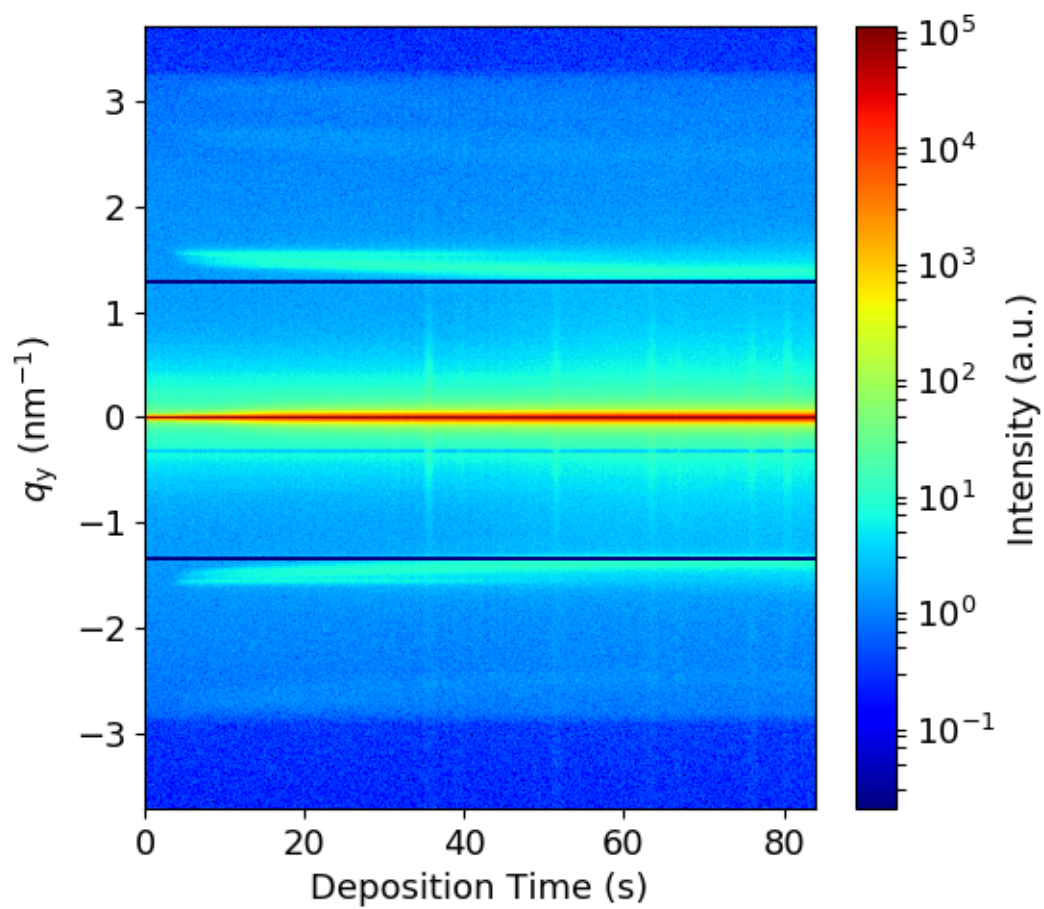


Figure S4: Contour plot of horizontal scattering profiles extracted from each frame versus deposition time for a Sol with OTAB.. Integrations were done at the Yoneda position of the TiN/silica sol interface at  $q_z=0.5 \text{ nm}^{-1}$ .

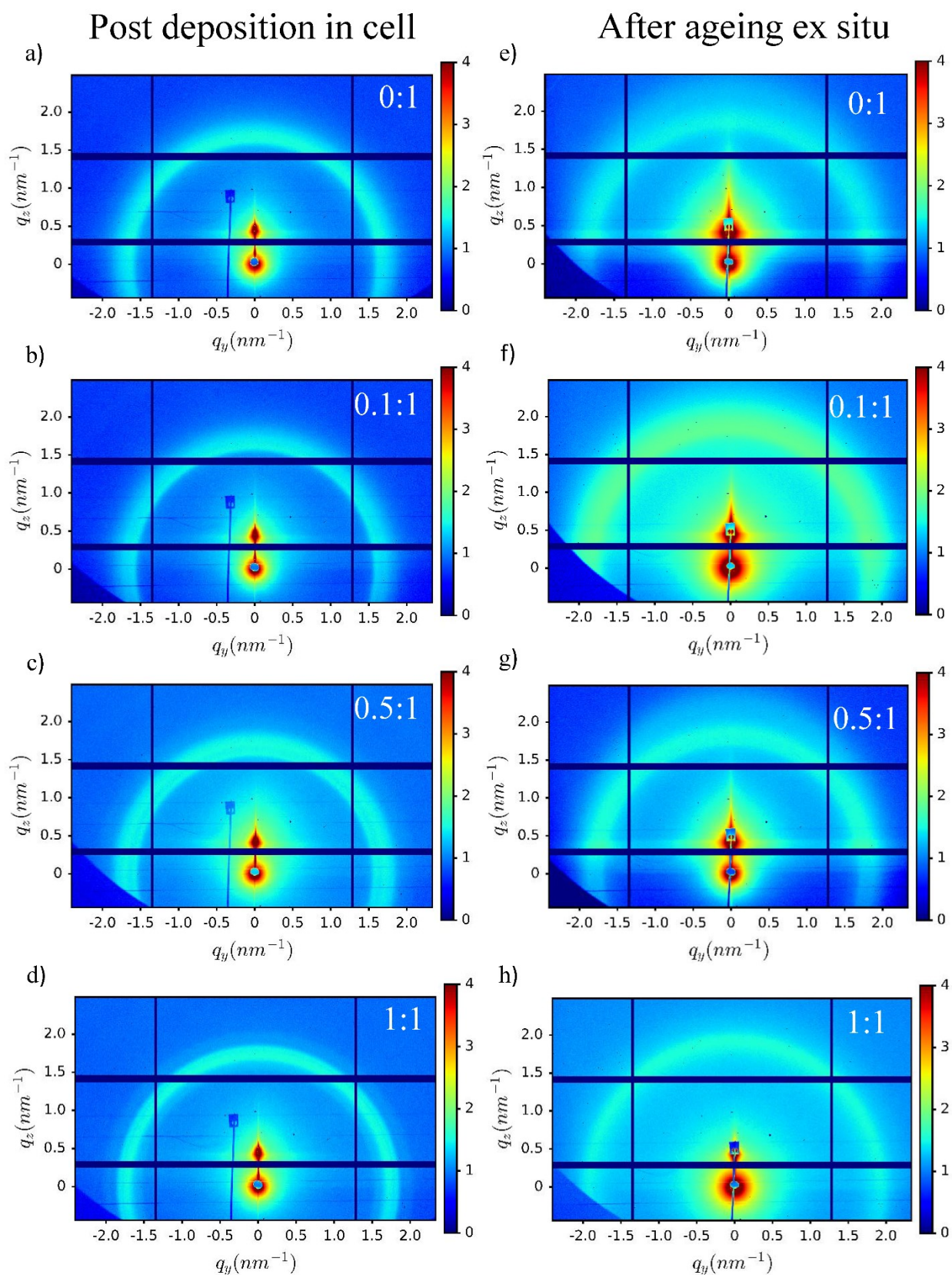


Figure S5: GISAXS images of silica samples taken a-d) after deposition ex situ and e-h) after ageing at 130° C overnight. The mesitylene concentration was varied versus [CTAB] as a,e) 0:1, b,f) 0.1:1, c,g) 0.5:1, and d,h) 1:1. Exposure time: 60 s, incident angle: 0.2°.

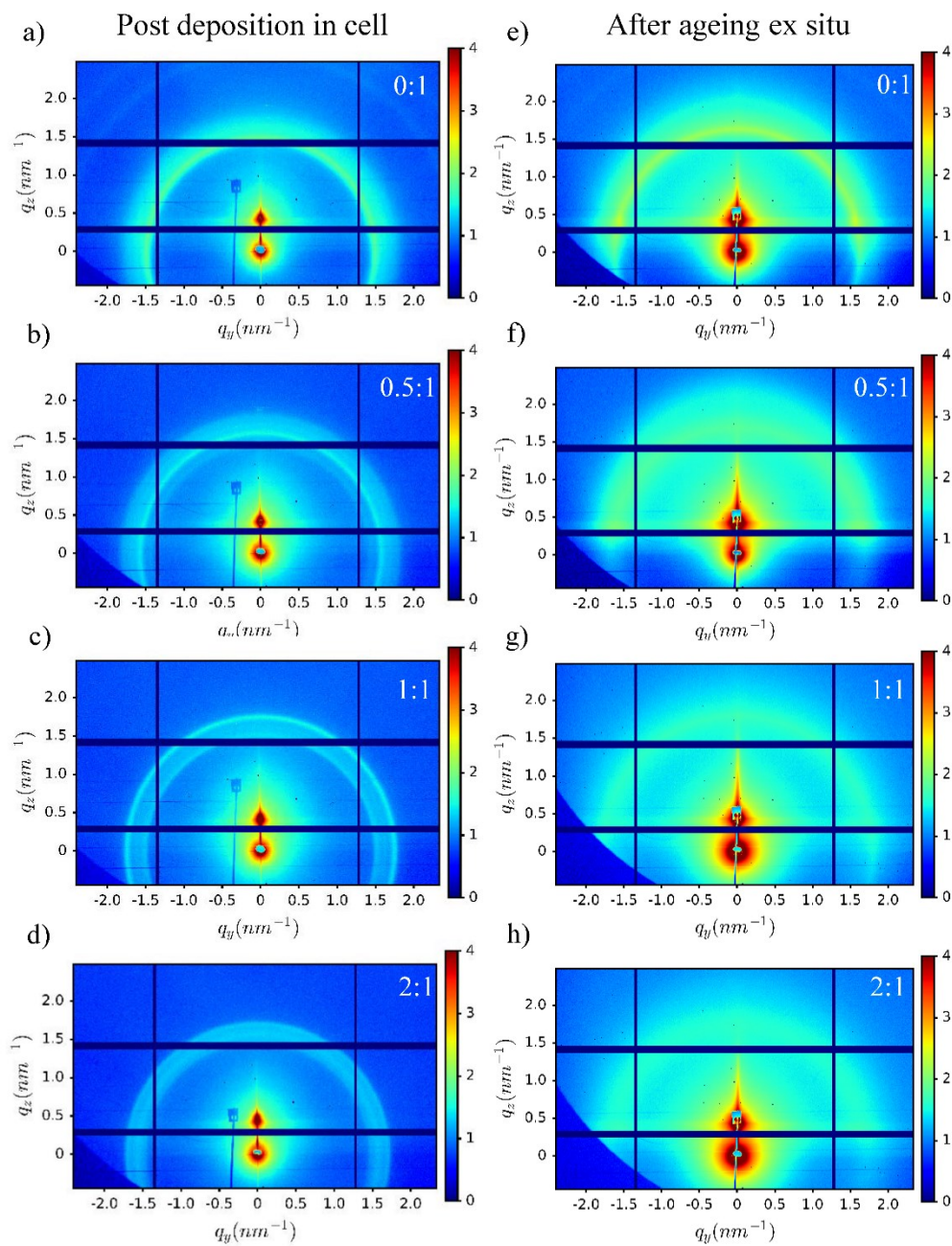


Figure S6: GISAXS images of silica samples taken a-d) after deposition ex situ and e-h) after ageing at 130° C overnight. The mesitylene concentration was varied versus [OTAB] as a,e) 0:1, b,f) 0.5:1, c,g) 1:1, and d,h) 2:1. Exposure time: 60 s, incident angle: 0.2°.

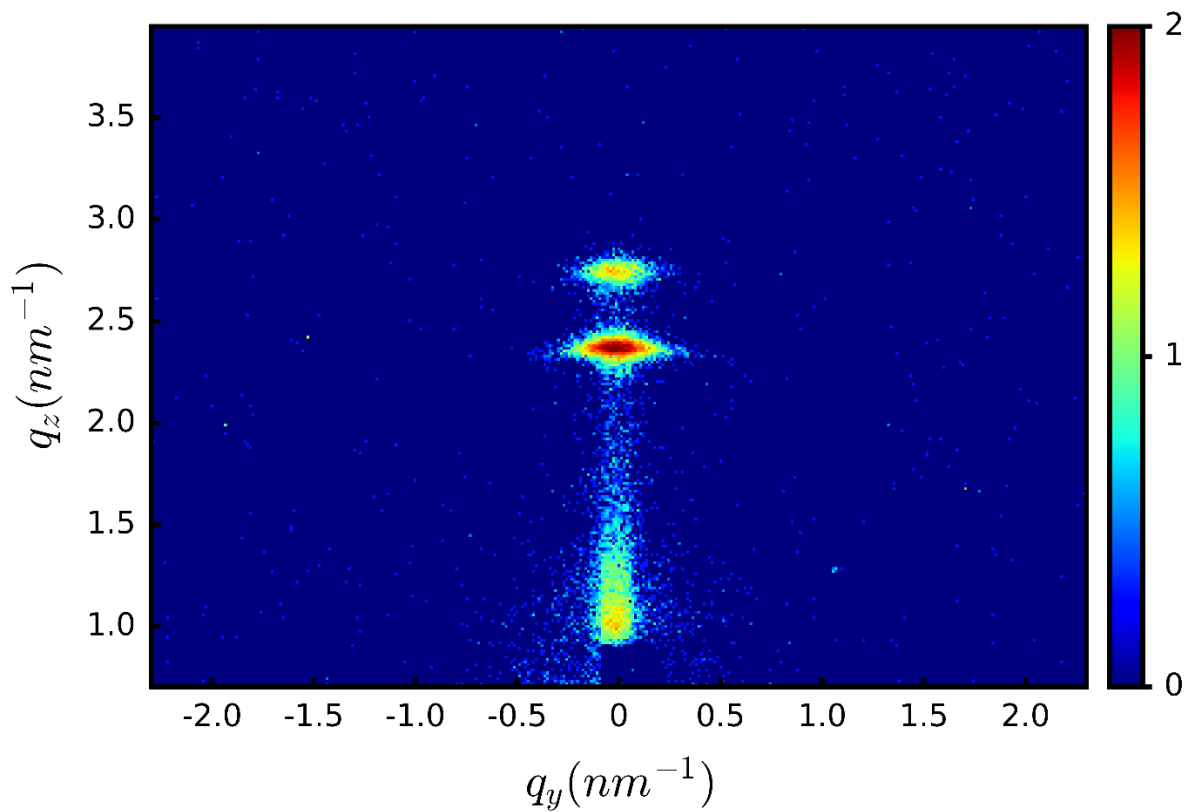


Figure S7: Scattering image of a TiN substrate dipped into a solution of 0.1 M NaNO<sub>3</sub>/EtOH (1:1) with CTAB (480 mg per 20 ml water) for a couple of minutes. Incident angle: 0.3°, exposure time: 600 s (Rigaku Smartlab).

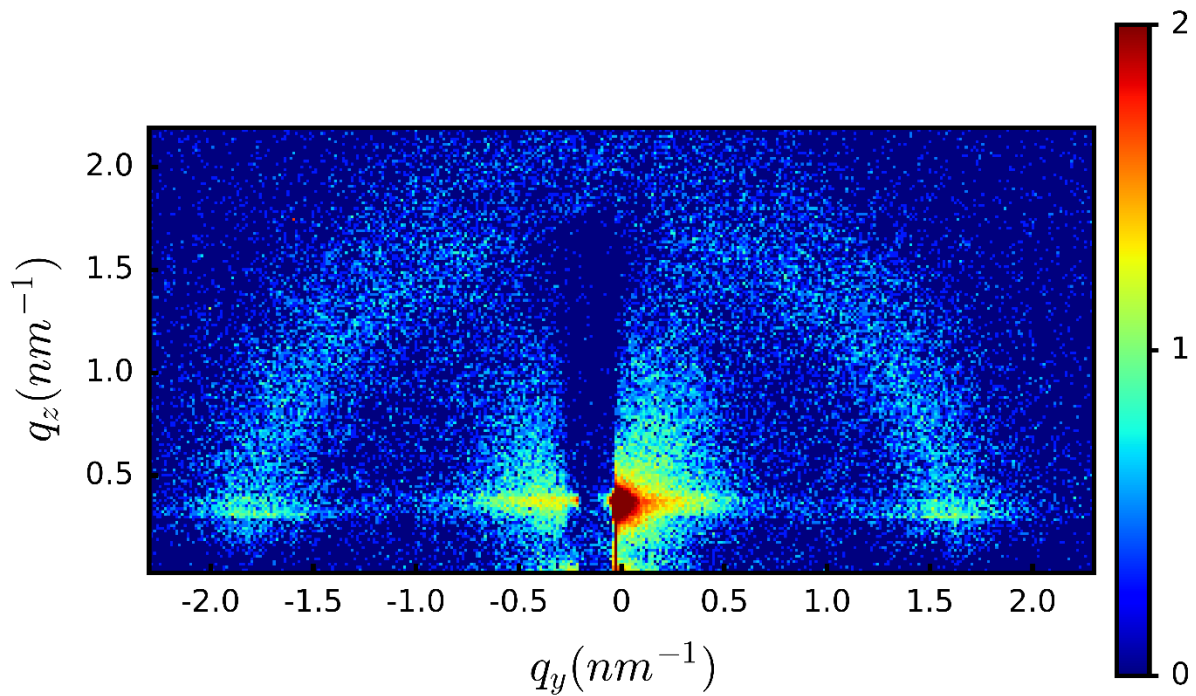


Figure S8: GISAXS image of a TiN substrate placed overnight into a solution of 0.1 M NaNO<sub>3</sub>/EtOH (1:1) with CTAB (480 mg per 20 ml water), followed by the addition of 905  $\mu$ l (per 20 ml water) and 12  $\mu$ l (per 20 ml of water) of 35 w% NH<sub>3</sub> solution. Incident angle: 0.3°, exposure time: 600 s (Rigaku Smartlab).

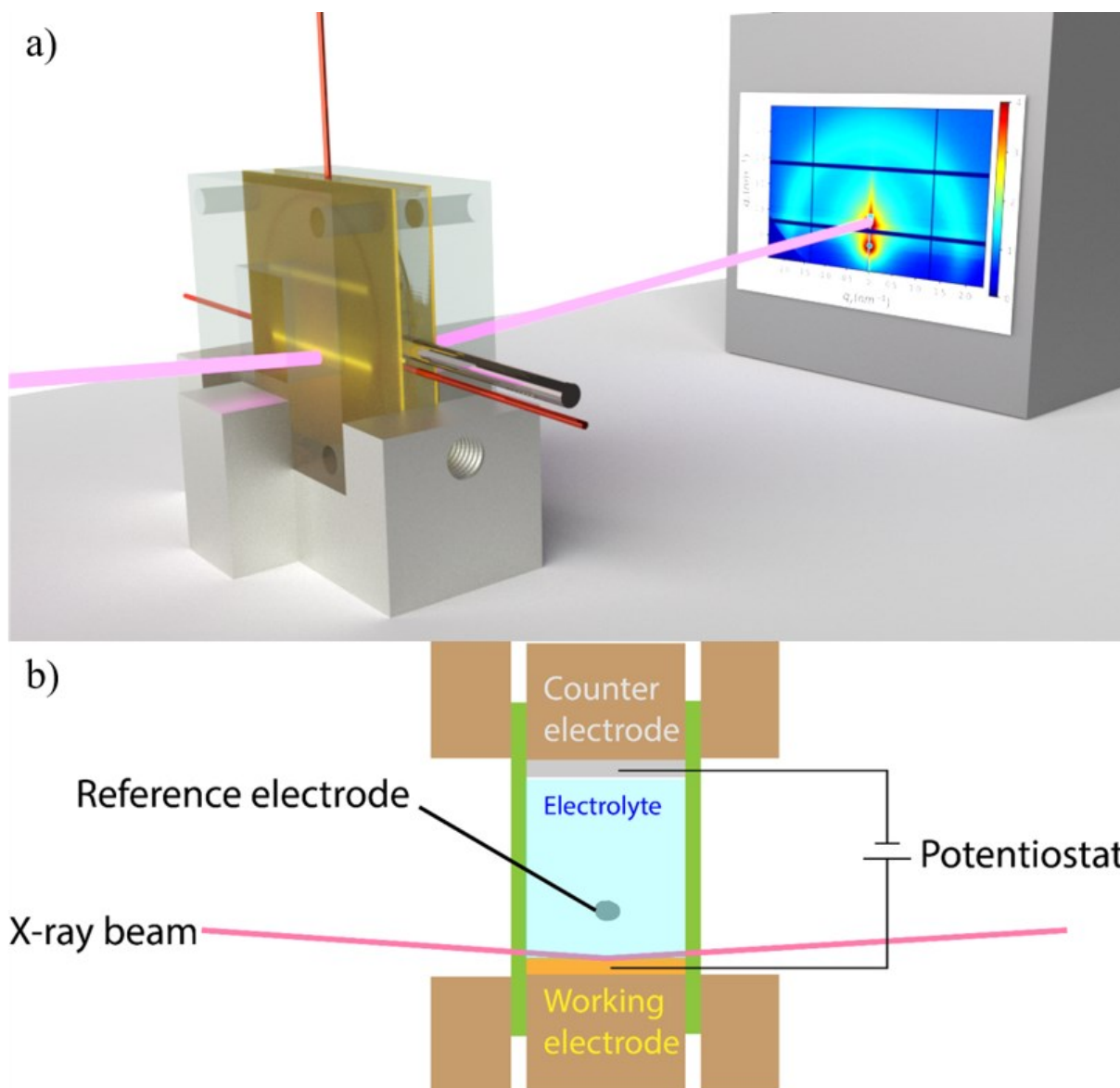


Figure S9: a) Illustration of the cell with the beam (pink) reflected at the substrate surface before reaching the detector. b) Schematic of the cell cross section, indicating the location of all electrodes/connections as well as the beam path. The TiN working electrode (orange) resides at the bottom of the centre part. On the opposite side, the Pt-gauge counter (grey) is placed in parallel for homogeneous deposition. The reference electrode (greyish spot) peaks in atop of the working electrode in order to reliably measure the working electrode potential. The outer cell parts sandwich one piece of Kapton foil (green) to each side of the inner cell part, sealing the cell while remaining optically transparent.

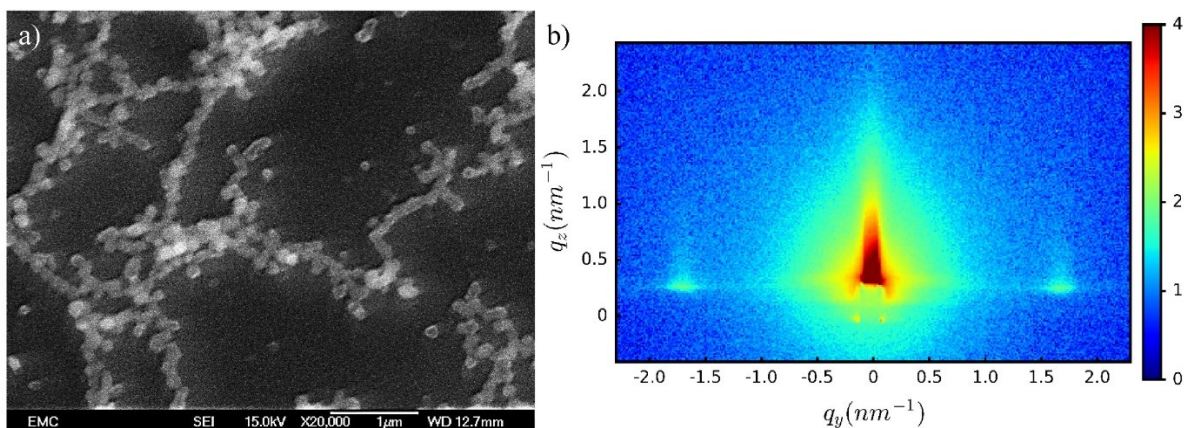


Figure S10: a) SEM and b) GISAXS image of a silica deposited onto TiN using a potential of -2 V for 2 s. GISAXS measurement done in house on Rigaku Smartlab.

### Swelling Study using Mesitylene:

As shown in **Table 1** of the manuscript, three different concentrations of mesitylene were used. From previous experiments, it was known that micelle swelling cannot be done indefinitely,<sup>1</sup> meaning that no vertically aligned channels were formed when exceeding a certain concentration of mesitylene. At equal molar concentrations of CTAB and mesitylene (1:1), a collapse of the vertically aligned pore structure was seen in the microscopy, verified by the lack of a corresponding GISAXS signal. The question arising from this was, whether the surfactant assembly would not happen at all due to the disturbance by the large amount of swelling agent or whether it would still form initially and only collapse during the deposition. **Figures S5 a-d)** display GISAXS images taken right after silica deposition with the sample still inside the cell. A strong semicircle feature can be seen in all images, indicating the formation of spheroid particles in the bulk solution, which totally dominate the scattering signal as long as the substrates reside in solution. For the aged samples shown in **Figure S5**, one can see that the films with ratio of (mesitylene:CTAB) **e)** 0:1, **f)** 0.1:1 and **g)** 0.5:1 show two spots in the horizontal plane in convolution with the strong semicircle, while the one with the maximum amount of mesitylene (**Figure S5 h)**) does not show that feature. This could mean that no vertically aligned pores were formed in the latter case. **Figure S11 a)** shows the horizontal scattering profiles post deposition, **b)** after ageing in the horizontal plane and **c)** their corresponding real-space values obtained for increasing amounts of mesitylene concentration and CTAB as the surfactant. The graphs show that until reaching a ratio 0.5:1, the inter-domain spacing increases slightly, starting from 3.55 nm to 3.63 nm. Surprisingly for the 1:1 ratio, the spacing decreases to a value lower than without the swelling agent. The scattering signals do also become broader when [mesitylene] is increased, indicating an overall loss of order.



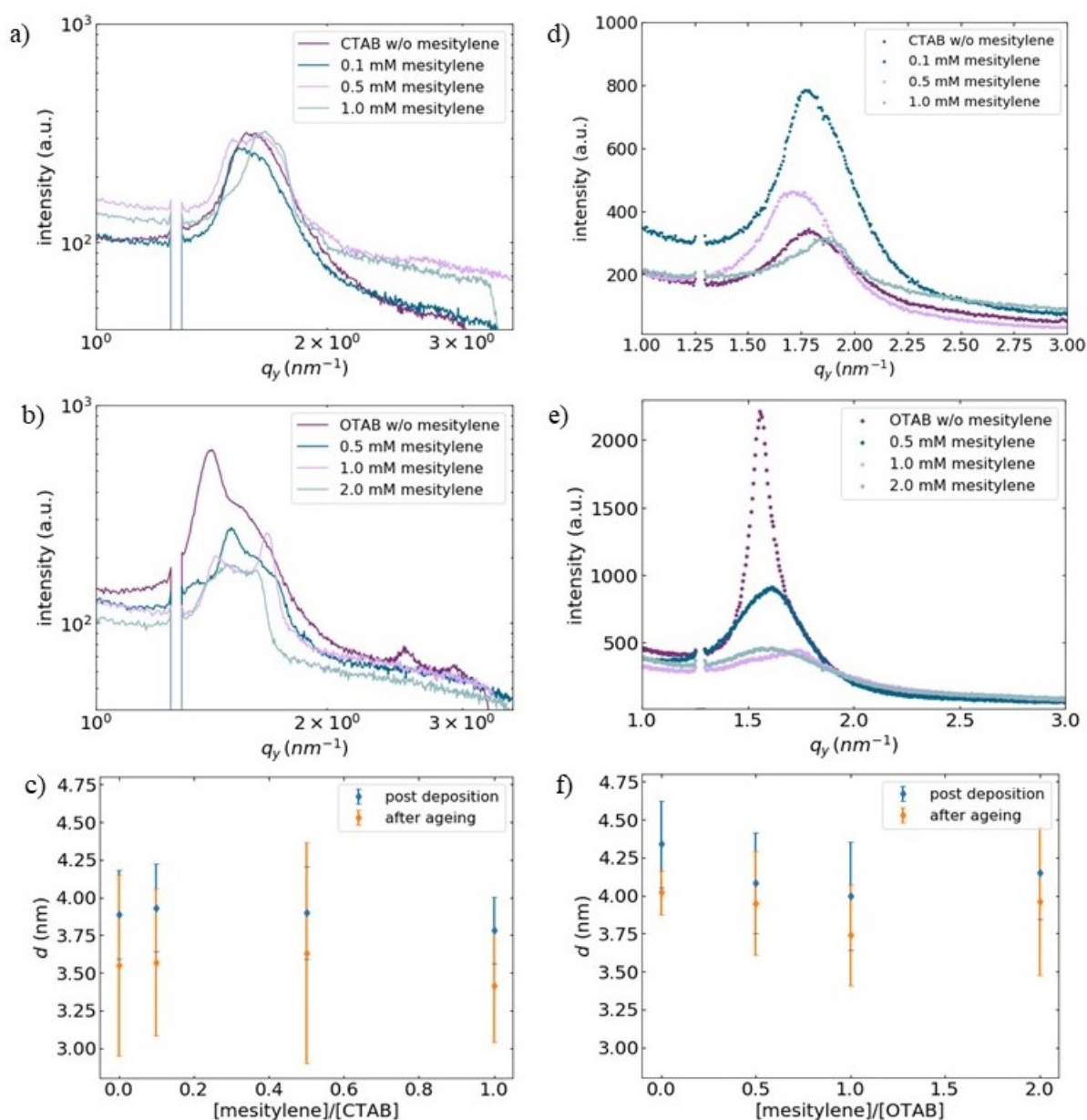


Figure S11: Horizontal scattering profiles of the silica structures a,d) post deposition (still in the cell), b,e) after ageing with increasing amounts of mesitylene concentration using CTAB/OTAB respectively. c,f) Real space values corresponding to the peaks shown in a,d) and b,e).

The effect of the different amounts of swelling agent on the actual peak positions fitted using the previously introduced twin Gaussian function, is shown in **Figure S12**. The curves gradually shift to lower  $q_y$  values with increasing ratio of [mesitylene:CTAB] (**Figure 12 a-c**), while the one with a ratio of 1:1 (see **Figure S12 d**) only had the semicircle as a visible feature. The inflation of the structure does also seem to be a lot weaker in this measurement than in the ones with lower amounts of mesitylene. The best fit with continuous positions of two peaks was obtained for a ratio of 0.1:1 shown in **Figure S12 d**. **Figure S12 b**) shows how the algorithm lost track of one of the shapes as they are practically merging, causing the false detection of background noise as a second peak at depositions times larger than 40 s, where the blue curve makes an abrupt change to higher  $q$  values again. In **Figure S12 c**) one can see that another peak was tracked with a much higher  $q$  value than seen previously, as it was not possible to deconvolve two peaks in the main signal around  $1.62 \text{ nm}^{-1}$ . This peak could correspond to a higher order peak of the observed structure, but is most likely the

result of false tracking due to the fitting algorithm reaching a local convergence minimum. The presence of mesitylene could inhibit the diffusion of ethanol (mentioned in<sup>2</sup>) into the micelles as vital for the vertical pore alignment) and hence the formation of vertically aligned channels as a film. This would fit well with the observation that the amount of inflation in the structure diminished with increasing content of swelling agent.

The swelling experiments were also repeated using OTAB as the surfactant. Otherwise, all conditions were kept the same as previously, excluding a slight variation of the concentration ratios between mesitylene/OTAB (as shown in **Table 1**). 2D scattering images of the sample after deposition as well as after ageing are summarised in **Figure S6 a-d**) and **e-h**) respectively. Similarly, as for the CTAB experiments, the images taken in the cell after deposition are dominated by the semicircle features from particles in solution, while the aged samples also possess a horizontal feature. **Figure S11** shows the lateral peak profiles **d)** post deposition, **e)** after ageing and **f)** their corresponding pore distances  $d$  for increasing amounts of mesitylene (0, 0.5, 1.0, 2.0/CTAB). Previously it was shown that the use of OTAB instead of CTAB leads to a larger pore structure (with no swelling agent present). The introduction of mesitylene to this system leads most strikingly to a broadening of the scattering peaks, where the Gaussian curves fitted to those suggest that the pore spacing actually decreases when increasing the amount of added mesitylene up to 1:CTAB, after which it returns to a centre value close to the one at 0 concentration, but with at least double the width. The accuracy of the peak position dramatically decreases with increased amounts of swelling agent, showing that its addition mainly leads to a decrease in the degree of ordering within the film structure, and not to a significant increase in pore size.

As done for the CTAB experiments, the lateral peaks in the two-dimensional images were tracked using a twin Gaussian peak function, of which the results are shown in **Figure S12** for **d)** 0.5:1, **e)** 1:1 and **f)** 2:1 of mesitylene:OTAB present in the sol (solutions B2-B4 in **Table 1**). Here, double peaks were successfully tracked for all data sets, except for the first  $\approx 17$  s of the experiment done with sol B3 (**Figure 6e**). The degree of inflation seems to be less and less with increased amount of mesitylene again, as seen in the previous section on CTAB. The persistence of this behaviour indicates its relation to the presence of mesitylene in the sol, with the actual surfactant chain length being of less importance.

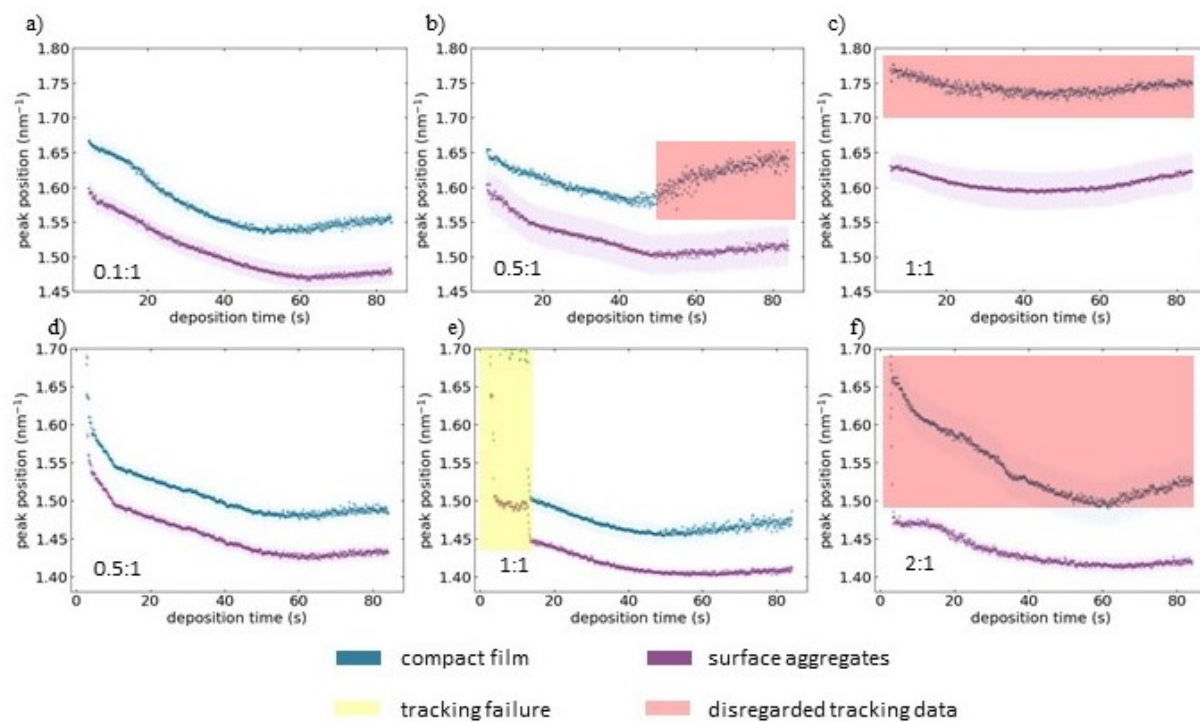


Figure S12: Peak positions of horizontal scattering features tracked using a twin gaussian function for different amounts of mesitylene using CTAB/OTAB as surfactant. Mesitylene:CTAB ratios are a) 0.1:1, b) 0.5:1 and c) 1:1. Mesitylene:OTAB ratios are d) 0.5:1, e) 1:1, f) 2:1.

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2 X. Zhang, Y. Dou, C.-Y. Mou, A. M. Asiri, Z. Teng, W. Li, G. Zheng and D. Zhao, *Angewandte Chemie International Edition*, 2012, **51**, 2173–2177.