In-situ sol-gel templating in a micro-fluidic cell probed at beamline P03 (PETRA III)

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Crystalline titania is a widely investigated inorganic semiconductor, which is of interest for example in photocatalysis and photovoltaics. Among its many advantages are low cost and easy producibility. The disadvantage of a necessary high temperature step can be circumvented by the usage of a novel titania precursor. One possible precursor for titania which does not require a high-temperature step to obtain crystallinity was previously used to create crystalline particles with the inverse microemulsion technique for usage in catalysis [1].

Nanostructuring of titania thin films is of great interest because for many applications a large surface area is crucial. One way to structure titania is the combination of the so called ‘good-poor’ solvent induced microphase separation of an amphiphilic block copolymer with sol-gel chemistry [2]. An amphiphilic block copolymer like poly(styrene-block-ethylene oxide) P(S-b-EO) is dissolved in a ‘good’ solvent that dissolves both blocks. By the addition of the titania precursor and hydrochloric acid, which is a ‘poor’ solvent for the PS-block, a microphase separation sets in, where the titania particles chemically coordinate to the PEO-block of the block copolymer. Sol-gel templating with a block copolymer has been shown to be successfully combined with micro-fluidics to produce more ordered titania structures because of the controlled reaction kinetics in the sol-gel [3]. The evolution of the structures in the sol-gel with the novel precursor was investigated in-situ with grazing incidence small angle X-ray scattering (GISAXS) at the beamline P03 at the storage ring PETRA III. A micro-fluidic cell made from TOPAS was put on a pre-cleaned glass substrate [4]. The evolution of structures on the glass substrate in the channel was probed. Synchrotron radiation with a wavelength of 0.0969 nm, a beam size of 20×40 µm^2 (vertical × horizontal direction) and an incident angle of 0.43° on the surface of the films was used for the measurements. The sample-to-detector distance at P03 was set to 2.5 m. The scattered signal was detected with a two-dimensional Pilatus 300k detector with 487×619 pixels of a pixel size of 172×172 µm^2 and an active area of 83.8×106.5 mm^2 with no read-out noise.

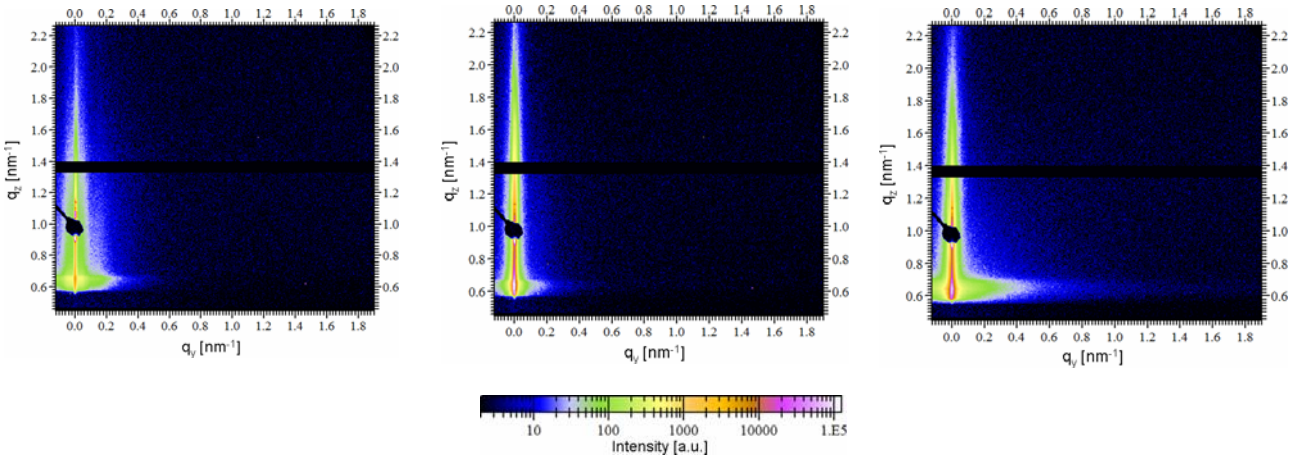

Figure 1: *Selected GISAXS scattering patterns at a fixed position in the micro-fluidic cell: from left to right frame 1, 750 and 2700 are shown.*

Figure 1 shows three selected 2d GISAXS scattering patterns at a fixed position in the channel of the micro-fluidic cell. For this experiment a solution of the block copolymer P(S-b-EO) was injected at one inlet of a y-shaped channel, the dissolved titania precursor was injected on the other inlet. The measurement time for each frame was 0.5 s. Frame 1 shows the scattering pattern of the cell on the glass substrate before injection. Frame 750 is representative for scattering patterns after infusion of the sol-gel components into the channel and frame 2700 shows a scattering pattern in equilibrium after the sol-gel particles have settled on the surface of the glass substrate. At frame 2700 the flow in the channel was stopped and the sol-gel was allowed to sediment.

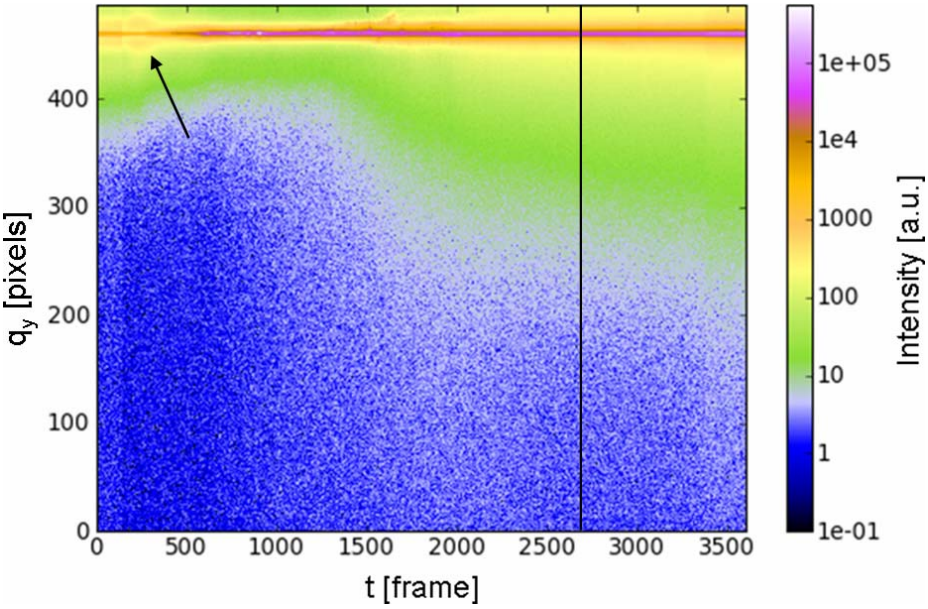

Figure 2: *Evolution of intensity along q_y at a fixed q_z-value over time. The black line indicates the stop of flow through the micro-fluidic cell at frame 2700.*

For an illustration of the evolution of structures on the glass substrate during mixing of the sol-gel in the micro-fluidic channel the intensity along q_y at a fixed q_z-value is shown over time in figure 2. Until about frame 100 no fluid is present in the channel, the scattering originates solely from the glass substrate and the micro-fluidic channel. Larger structures, indicated by an arrow in figure 2, show up shortly after infusion, but disappear again quickly. The intensity scattered in q_y-direction decreases when the fluid enters the cell. After some time, approximately at frame 1500, particles in the sol-gel begin to form and sediment on the glass substrate. The equilibrium is already reached at around frame 2200, which corresponds to 1100 s after the start of the injection and just 350 s after the start of the sedimentation.

In conclusion, the very promising combination of micro-fluidics and block copolymer templated sol-gel chemistry was successfully demonstrated in-situ with GISAXS at the PETRA III beamline P03. The kinetics of structures formation in the sol-gel process is investigated with a high time resolution.

References

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