ESRF	**Experiment title:** Orientation of nanochannels in a confined silica-based mesophase by micro X-ray diffraction	**Experiment number**: HS-3727
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Report:

1. Aim of the experiment (in synthesis)

The expeimet was conceived within our research activities of characterization of mesostructured silica monoliths grown inside quartz micro-capillaries. These materials are synthesized by filling the capillaries with silica mesophase solution, which through self-assembly under proper conditions drives the formation of a mesostructured phase, (possibly) characterized by continuous, long-range ordered and crack-free nanochannels.

In the experimental session at ESRF we aimed at exploiting the ID13 beamline to investigate by transmission micro X-ray diffraction (micro-TXRD) with micrometer spatial resolution the presence and orientation of these nanochannels. The specific goal was to evaluate the influence of the synthesis parameters on the channel orientation in order to set the optimal ones to obtain a confined silica-based nanostructure with a high degree of nanochannel orientation.

A preliminary measurement at ID13 indicated that the planned experiments were feasible and that they could give the desired information.

Further details on the aim of the experiment and on the scientific background are given in the proposal.

2. Materials and methods

2.1. Sample preparation

A set of 32 samples synthesized under different conditions was prepared. In particular, the mesophase synthesis was performed by following 4 procedures, characterized by different source of silica, surfactants (as structural-directing agent) silica/surfactant ratio and solution pH. Furthermore, for each procedure, the conditions of the *ageing* phase in terms of time, temperature and controlled atmosphere were also varied one at a time. A summarizing table of the synthesized samples is reported below.

For all the synthesis, the capillary tubings (internal diameter of 3 μm and the external diameter of 120 μm) were immersed in the as-prepared synthesis solutions and all of the volatile solvent was removed in vacuum using a rotary evaporator at 40 °C for 25 min. This was carried out in order to facilitate filling of silica sols into the tubings and to reduce the time needed for gelation.

Synthesis	Sample Number	Ageing Parameters
P123, EtOH, HCl (1M), TEOS	1	Aged for 96 hours at RT in 40% humidity, then for 18 hours at 60°C
	2	Aged for 96 hours at RT, then for 18 hours at 60°C
	3	Aged in solution for 12 hours at 60°C
	4	Aged in solution for 12 hours at 60°C, then for 18 hours at 60°C in air
	5	Aged for 1 week at RT in 40% humidity
	6	Aged for 1 week at RT
	7	Aged for 1 week at RT in 40% humidity, then for 18 hours at 60°C
F127, EtOH, HCl (pH =1.43), TEOS	8	Aged for 96 hours at RT in 40% humidity, then for 18 hours at 60°C
	9	Aged for 96 hours at RT, then for 18 hours at 60°C
	10	Aged in solution for 12 hours at 60°C
	11	Aged for 1 week at RT in 40% humidity
	12	Aged for 1 week at RT
	13	Aged for 1 week at RT in 40% humidity, then for 18 hours at 60°C
F127, EtOH, HCl (pH =1.4), TMOS	14	Aged for 96 hours at RT in 40% humidity
	15	Aged for 96 hours at RT
	16	Aged in solution for 12 hours at RT
	17	Aged for 96 hours at RT in 40% humidity, then for 18 hours at 60°C
	18	Aged for 96 hours at RT, then for 18 hours at 60°C
a) CtABr, EtOH, HCl (0.2M), TEOS b) P123, NaCl, EtOH, HCl (0.2M), TEOS c) P123, EtOH, HCl (0.2M), TEOS	19	Synthesis b Aged in solution for 12 hours at 60°C
	20	Synthesis c Aged in solution for 12 hours at 60°C
	21	Synthesis b Aged for 12 hours at RT in 40% humidity
	22	Synthesis c Aged for 12 hours at RT in 40% humidity
	23	Synthesis b Aged for 12 hours at RT
	24	Synthesis c Aged for 12 hours at RT
	25	Synthesis a Aged for 12 hours at RT in 40% humidity
	26	Synthesis a Aged for 12 hours at RT
	27	Synthesis a Aged for 12 hours at RT in 40% humidity, then for 18 hours at 60°C

	28	Synthesis a Aged for 12 hours at RT, then for 18 hours at 60°C
	29	Synthesis b Aged for 12 hours at RT in 40% humidity, then for 18 hours at 60°C
	30	Synthesis c Aged for 12 hours at RT in 40% humidity, then for 18 hours at 60°C
	31	Synthesis b Aged for 12 hours at RT, then for 18 hours at 60°C
	32	Synthesis c Aged for 12 hours at RT, then for 18 hours at 60°C

2.2. Micro TXRD experiments

The samples (capillary tubings loaded with the mesostructured silica) were mounted, with a parallel alignment, on the sample holder of the scanning diffractometry set up and aligned with the axis perpendicular to the microbeam (1.2 x 1.0 μm^2). Each diffraction pattern was collected for 3 seconds using X-rays of wavelength λ = 0.0996 nm. Y scanning of the samples was performed with a step size of 1 μm at different positions along the Z axis of the capillary (Z step size = 40 μm), see also Fig. 1.

The two-dimensional data were corrected (detector projection and background subtraction) and processed using FIT2D (www.esrf.eu/computing/scientific/FIT2D/).

3. Results and discussion

In the experimental session we measured all the 32 prepared samples. Unfortunately, the experiments did not sort the desired results.

In Fig. 1 it is showed a representative result of (unfortunately) all the measurements we performed, it refers to sample No. 1. In the left hand panel it is reported the optical image of sample (the capillary has an internal diameter of 3 μm and the external diameter of 120 μm), while the reconstructed image of the significant micro-TXRD patterns is shown in the right hand panel. The patterns refer to the internal area of the capillary tubing, where the mesostructured silica monoliths was expected to be. We see that some of the patterns (a sample one is yellow squared) present a Debye's ring related to domains characterized by the coherent repetition of 10 nm distant planes, thus suggesting the presence of nanochannels of this size. This feature is the one expected to be produced by the X-ray scattering of randomly oriented nanochannels of the silica mesophase. However their spatial distribution does not match the rectangular 2D geometrical projection of the internal channel of the capillary tubing, as evidenced in the figure by the black dotted reference lines. To the contrary some patterns that present only the features of the X-ray scattering of the quartz walls and of the beam stopper were obtained from regions corresponding to the internal channel of the capillary tubing (a sample one is green squared). These results suggest that the mesostructured silica monoliths were not synthesized inside the microcapillary tube, but insted onto its outside surface.

To unambiguously confirm this hypothesis we performed micro-TXRD experiments on several samples after they were washed in acetone (full immersion for 1 h) in order to remove any impurity or coating eventually adsorbed onto the outside surface of the capillary tubing. In Fig. 2 it is showed the result related to sample No. 1, that is a representative result of all the analogous experiments we conducted. As in Fig. 1, in the left hand panel it is reported the optical image of the sample, while the reconstructed image of the significant micro-TXRD patterns is shown in the right hand panel. We see that the optical image evidences a clean, transparent quartz capillary tubing with respect to the optical image reported in Fig. 1. Regarding the micro-TXRD patterns, in the top y raw, which is related to the void region atop of the capillary tubing, they only present the black dot of the beam stopper, as obvious. In the bottom y raw, corresponding to the capillary tubing, they present the features of the quartz wall, but the Debye's ring related to the silica nanochannels are always missed. This implies that the acetone treatment washed out the material responsible for the Debye's ring displayed by some of the patterns shown in Fig. 1. After merging information and arguments related to Fig. 1 and Fig. 2 it is evident that the synthesis produced non-uniform films of silica adsorbed onto the outside surface of the capillary tubing, characterized by randomly oriented nanoperiodicities (probably nanochannels) of 10 nm size.

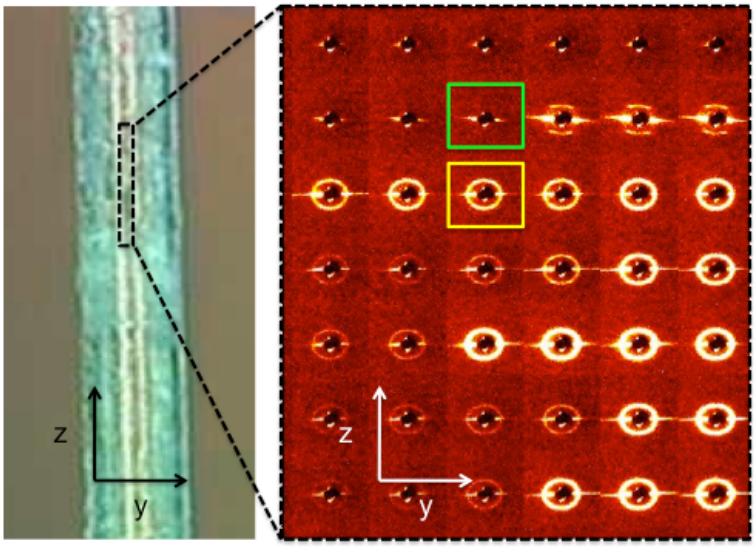

Fig. 1. Representative micro-TXRD experiment (sample No. 1). Left hand panel: optical image of the sample (the capillary tubing has an internal diameter of 3 μm and external diameter of 120 μm). Right hand panel: reconstructed image of the transmission micro-TXRD patterns related to the internal area of the tube evidenced by the dashed black square (microbeam size 1 μm^2, y scan step = 1 μm, z scan step = 40 μm. Note that the reconstruction does not take into account the different scan steps in z and y). The green squared pattern presents the features of the X-ray scattering of the quartz walls and of the beam stopper, the yellow squared one also presents a Debye ring related to randomly oriented nanochannels of 10 nm average size.

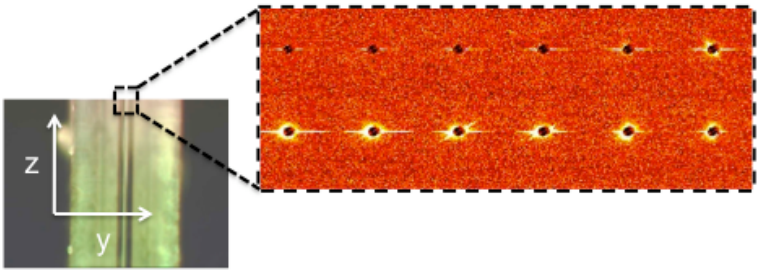

Fig. 2. Representative micro-TXRD experiment after acetone treatment (sample No. 1). Left hand panel: optical image of the sample (the capillary tubing has an internal diameter of 3 μm and external diameter of 120 μm). Right hand panel: reconstructed image of the transmission micro-TXRD patterns related to the area evidenced by the dashed black square (microbeam size 1 μm^2, y scan step = 1 μm, z scan step = 40 μm. Note that the reconstruction does not take into account the different scan steps in z and y). The patterns of the top y raw only display the beam stopper black dot, the patterns of the bottom y raw also display the scattering features related to the quartz walls of the capillary tubing.

4. Conclusions and perspectives

The experimental session did not sort the wanted results because the sample set did not present the expected characteristics. Instead of being mesostructured silica monoliths confined inside the quartz micro-capillary and characterized by long-range ordered nanochannels, they resulted in a non-uniform silica coating of the capillary tubing outside surface, characterized by randomly oriented nanochannels (of 10 nm average size).
This result was unexpected also because the synthesis protocols were set according to the ones that produced the sample analyzed in the preliminary successful experiment. Work is in progress in order to understand where the synthesis failed and to eventually redesign it. A continuous feedback control of the synthesized samples by transmission and scanning electron microscopy has also been implemented.
After fixing this aspect, a new proposal for micro-TXRD experiments at ESRF ID13 will be submitted.