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Supporting Information

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Fluid Flow Control in Cotton Threads with Mesoporous Silica Coatings

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Dense and mesoporous silica coating on cotton threads

The modification of the thread wettability and with this the adjustment of the intrinsic microfluidic fluid flow was achieved with the deposition of dense or mesoporous silica coatings. Therefore, cotton threads were cut into 6 cm long pieces and clamped into a sturdy holder. Due to the placement into a holder the threads get stretched which ensures a complete immersion of the thread during the coating procedure and a homogenous coating distribution. Up to the modification the threads get dipped into the corresponded sol-gel solution and were withdrawn with a constant withdrawal speed of 2 mms^{-1}. The dip-coating procedure was performed under norm condition (relative humidity of 50 ± 5 % and a temperature of 25 ± 1 °C), which ensures the mesopore formation during the dip-coating and is based on the evaporation-induced self-assembly process (EISA). After the coating, the freshly modified threads are aged under the same norm conditions before they undergo a thermal post-treatment up to a final temperature of 130 °C which is kept for 2 h. As we observed by TGA measurements a temperature of 300 °C or higher leads to the combustion of the organic thread material. Threads coated with sol-gel solution containing the mesopore forming template Pluronic® F 127 need to be stored in a 0.01 M acidic ethanol bath for 3 days to extract the template and to create the pores in the silica-coating. Figure S 1 shows the single steps for applying a dense or a mesoporous silica coating at cotton threads.

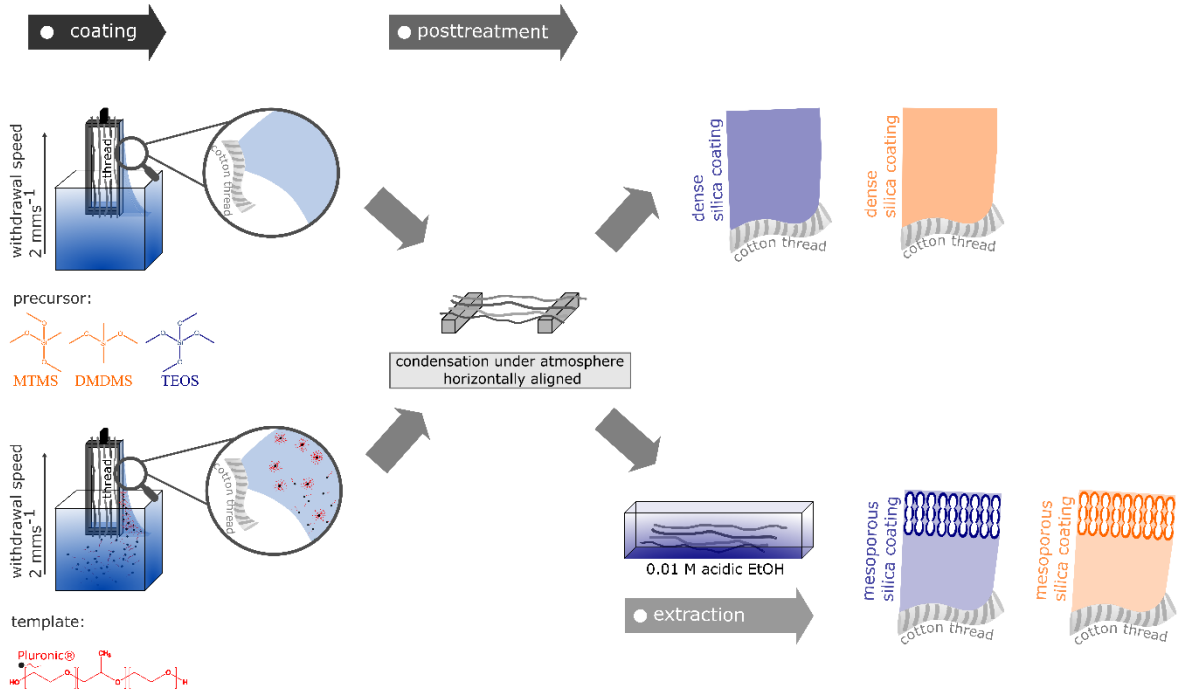


Figure S 1: Schematic illustration of the different process steps for the cotton thread modification with dense or mesoporous silica coatings.

Thread preparation before coating

The surface of commercially available unmodified cotton threads is in homogeneously hydrophobic and hydrophilic (Figure S 2 a). Hydrophobic areas at the thread can be caused by their fabrication in which wax films are applied at the surface or contaminations occur.[21] The intrinsic hydrophilicity of unmodified cotton threads is influenced by these impurities which prevents a homogenous imbibition of a water droplet (Figure S 2 a). Spots along the thread can be even hydrophilic, as their intrinsic wettability, or hydrophobic caused by the impurities (Figure S 2 a). To create homogenous wettability along the thread, the threads were treated with O_2 plasma (Femto, electronic diener, Nagold, Germany) before the dip-coating process was performed. The plasma treatment removes possible contaminations which leads to a homogenous wettability in every spot along the thread (Figure S 2 b).[2]; [21]; [17] Due to the O_2 plasma treatment the thread surface remains intact (Figure S 2 a and b SEM images).

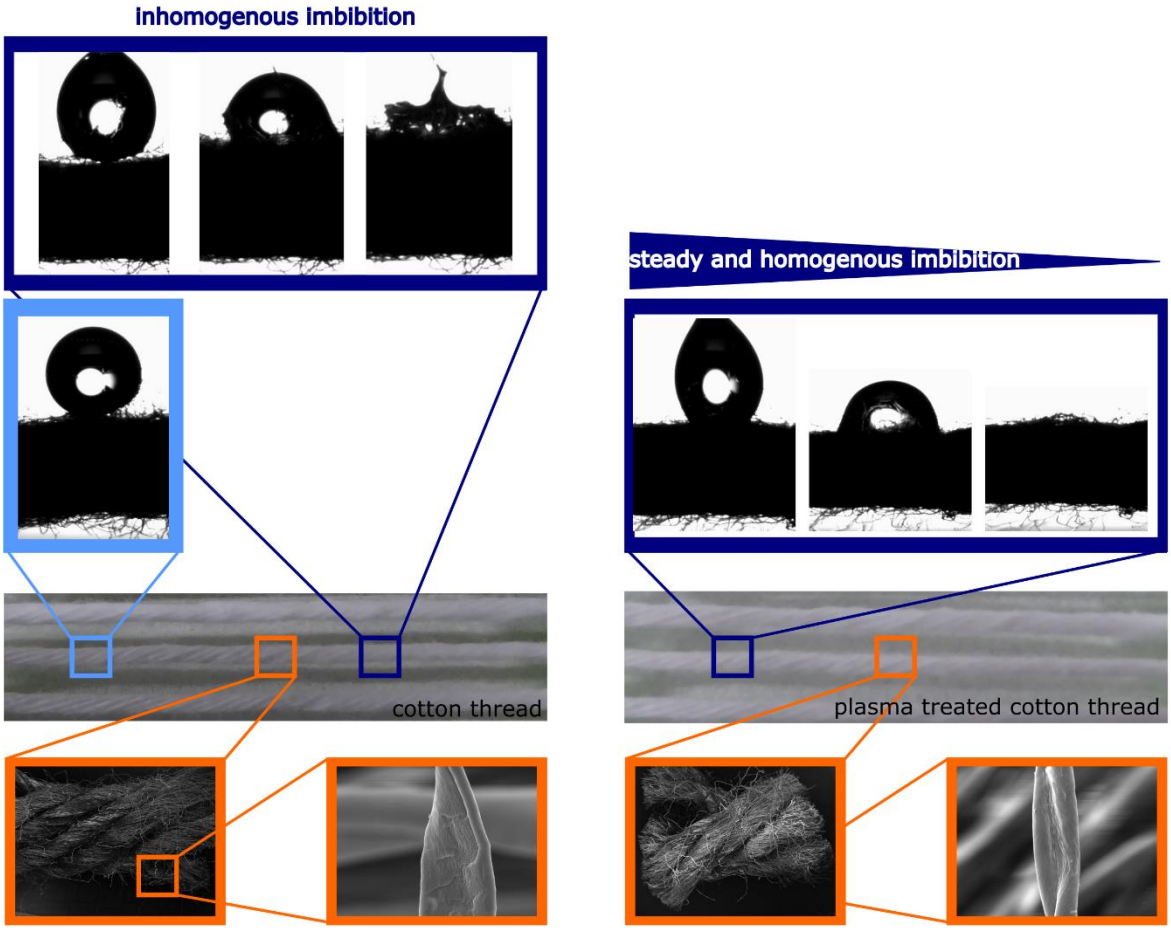


Figure S 2: a shows the inhomogeneity of commercially available cotton threads which leads to hydrophobic spots next to hydrophilic spots along the thread. b due to a water plasma treatment a complete hydrophilic thread is obtained without changing the thread surface texture.

Calculation of the silica-coating amount

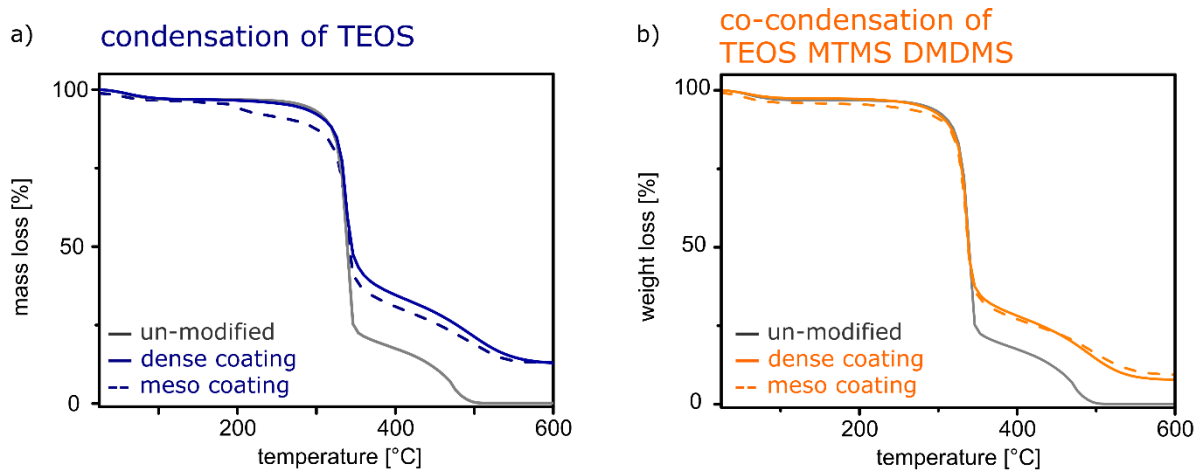
Silica is an inorganic compound which is stable even at high temperatures. To calculate the amount of the silica-coating in the cotton-thread-silica-hybrid material, the organic part of the hybrid-material can be calcinated and the residue amount is detected. In addition to the silica coating, ash remains after the thermal removal of the cotton thread. Based on this, the mass loss during the calcination of the cotton-thread-silica-hybrid material is subtracted from the mass loss of the unmodified cotton thread to obtain the amount of deposited silica-coating (Equitation 1). The values for the mass losses can be extracted from TGA measurements.

$$\boldsymbol{mass}\ [\%]_{\boldsymbol{deposit\ silica}} = \boldsymbol{mass\ loss}\ [\%]_{\boldsymbol{reference}} - \boldsymbol{mass\ loss}\ [\%]_{\boldsymbol{hybrid\ material}} \quad (1)$$

The silica formation as based on the hydrolysis and condensation of the silica precursor during the coating procedure and especially during the thermal post-treatment. The hydrolysis

and condensation of the precursor resulting in silica coating formation can in general affect the mass loss during the TGA measurements. In previous studies the temperature program with a final temperature of 130 °C (see Experimental Section) seemed to be sufficient to achieve complete condensation of the silica precursor. after the temperature treatment up to 130 °C solid-state NMR measurements showed the complete condensation of the silica precursor. Consequently, we assumed that a mass loss caused by hydrolysis and condensation of silica during the TGA measurement can be neglected and the amount of silica coating can be calculated using the equitation 1.[20]

Figure S 3 a and b show the TGA results for unmodified threads and for threads coated with dense or mesoporous silica. Up to the used coating and the TEOS concentration of the sol-gel solution, different amounts of silica are deposit. The coating amount for the four different coatings are summarized in Figure S 3 c. 13.6 ± 0.7 wt% is deposited onto the threat for the dense silica coating and 13.0 ± 0.5 wt% for mesoporous silica coating. For the dense silica coating containing MTMS and DMDMS 7.5 ± 0.1 wt% and for the mesoporous silica coating containing MTMS and DMDMS 10.3 ± 0.3 wt% silica are deposited. Thus, less silica is deposited for the coatings containing MTMS and DMDMS, which is ascribed to the lower TEOS concentration and the calcination of the organic groups of MTMS and DMDMS.



c)

	condensation of TEOS	co-condensation of TEOS MTMS DMDMS
dense	13.6± 0.7wt %	7.5 ± 0.1 wt%
meso	13.0± 0.5 wt%	10.3 ± 0.3 wt%

Figure S 3: a shows the TGA plots of unmodified threads as reference (grey plot), dense silica (blue plot) and mesoporous silica coated cotton threads (blue dashed plot). For the coating sol-gel solutions were used containing only TEOS as precursor. b shows the TGA plots for unmodified threads (grey plot) and threads with a mesoporous (dashed orange plot) as well as a dense (orange plot) silica coated thread whereby a sol-gel solution containing the precursors MTMS and DMDMS besides

TEOS. c Summary of the coating amounts deposit at the threads during dip coating in sol-gel solutions with different compositions.

Influence of different TEOS concentration on the silica-coating amount and thus on the wettability of the cotton thread

The TEOS concentration can be adjusted by using different TEOS to ethanol ratios. With increasing the TEOS : ethanol ratio the TEOS concentration decreases in the sol-gel coating solution. Based on this three sol-gel solutions with the TEOS ethanol ratio 1 : 20, 1 : 40 and 1 : 80 were prepared. The coating of the cotton threads was performed as described in the manuscript. After the coating the hybrid materials aged under norm conditions for 1 h before they underwent a thermal post-treatment with the final temperature of 130 °C. The silica coating amount was detected with TGA measurements whereby the temperature was increased from 25 °C to 600 °C with a rate of 10 °Cmin^{-1}. With the so-called highly concentrated sol-gel solution (TEOS : EtOH 1 : 20) a coating amount of 13.7 ± 0.7 wt% was obtained. When decreasing the TEOS concentration, which is the case for the TEOS : EtOH 1 : 40 sol-gel solution, 6.9 ± 0.3 wt% of silica is deposited onto the thread. This represents a 50 % reduction of the coating amount and is therefore proportional to the 50 % reduction of the TEOS concentration within the sol-gel coating solution. A further reduction of the TEOS concentration (TEOS : EtOH 1 : 80) results into a coating amount of 3.9 ± 0.7 wt%. Consequently, a linear relationship between TEOS concentration in the sol-gel solution and the deposited coating amount was observed.

Due to the silica coating the wettability of the threads changed from hydrophilic to highly hydrophobic. A static contact angle higher than 130 °and with this complete water exclusion is obtained for the threads coated with the high, intermediated or low TEOS concentrated sol-gel solution. Based on this results a coating amount of 4 wt% which can be realized with the low concentrated sol-gel solution (TEOS : EtOH 1 : 80), is sufficient to create e thread with water exclusion properties.

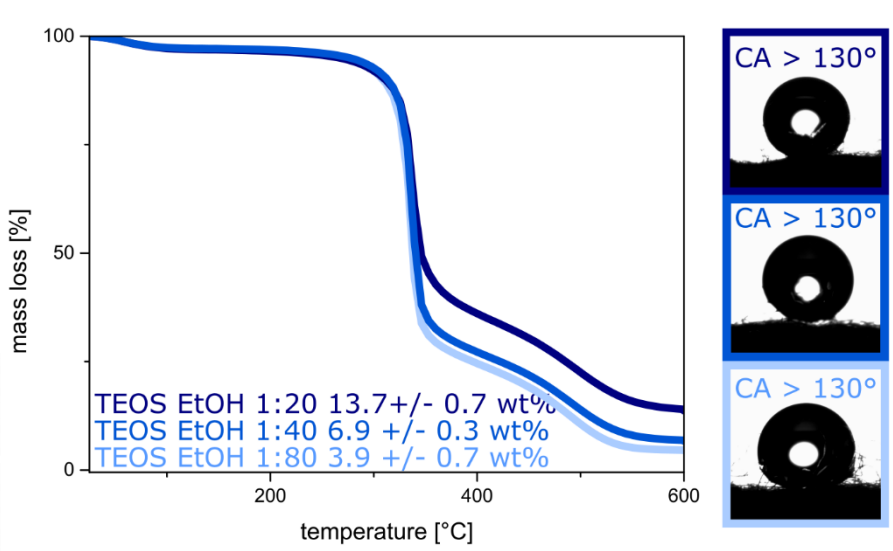


Figure S 4: a shows the TGA curves and the silica residues of cotton threads coated with sol-gel solutions containing different TEOS concentrations. b shows the contact angle in relation to the silica coating amount.

Coating distribution at the thread surface

To visualize the influence of the silica coating at the surface structure of the cotton thread as well as the silica coating distribution on the micrometer length scale SEM images and Confocal Laser Scanning Microscopy (CLSM) were performed (see **Figure S 5**). For CLSM imaging the cotton threads were stained with Calcofluor White (CFW) and the silica coating with rhodamine B (RhoB). The staining of the silica coating is based on the encapsulation of RhoB into the silica network during the condensation process. Therefore, 1 µM RhoB was added to the respective dip coating solution. Cotton threads were visualized in the xy- as well as in the z-plane to gain information of the coating distribution along the surface. Detecting CFW (in Figure S 5 g and h visualized in cyan) is ascribed by an un-coated part of the cotton thread, whereas the detection of RhoB (in Figure S 5 g and h visualized in magenta) is related to the silica coating.

When analyzing cotton threads at the micrometer scale the silica location along the thread surface and not on the single cotton fibers is analyzed. Comparing the SEM images of unmodified cotton threads at micrometer scale with the dense silica coated cotton threads, no change in the surface structure at micrometer scale is visible (see Figure S 5 b, e and i) although the silica coating is nearly distributed homogenously along the thread surface which is deduced from the CLSM images (see Figure S 5 g and h). Only a few single cotton fibers remain uncoated. The CLSM images show that with the dip-coating procedure a nearly homogenous silica coating at the thread surface is obtained without changing the surface structure at micrometer scale which is proved by the SEM images. The non-affection of the

fiber surface is most likely due to the minimal amount of deposited silica coating (see *Figure S* 2 a and d).

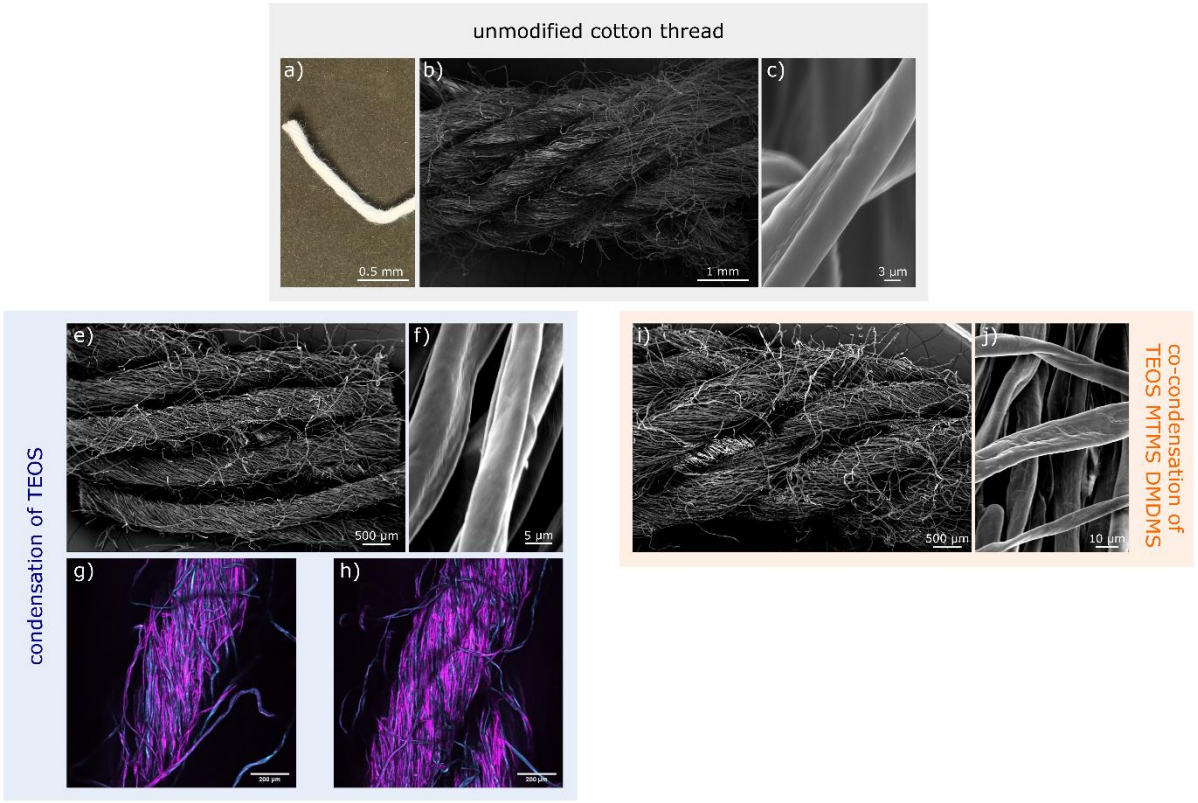


Figure S 5: a) shows an image of an un-modified cotton thread. e), f), i) and j) show SEM images with different resolutions of with dense silica coated cotton threads. g) and h) show the CLSM images of two different spots at a cotton threads with dense silica coating. The silica coating is visualized in magenta and the un-modified part of the cotton thread in cyan.[20]

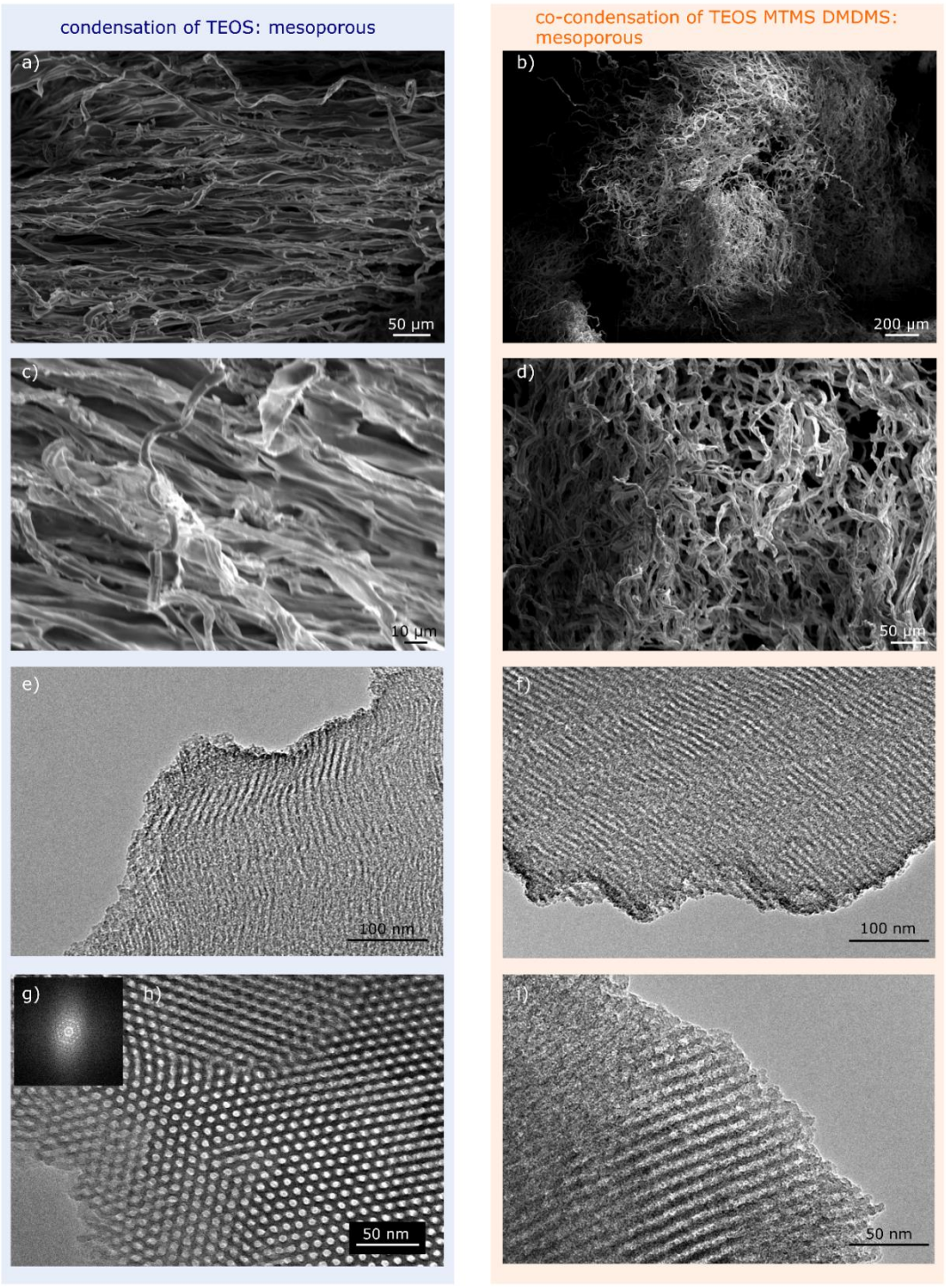


Figure S 6: a) – d) show SEM images with different resolutions of with mesoporous silica coated cotton threads after the thermal removal of the cotton thread. e) – f) show TEM images of the mesoporous silica coating.

Differences between the water and oil uptake up to the silica coatings

Due to the different silica coatings threads with a hydrophobic character can be obtained. Threads with a highly hydrophobic wettability show static contact angles higher than 130 ° and no water uptake is possible when placing them in a water reservoir for 2 min and weighing them afterwards. This is the case for threads with a dense silica coating. Nonpolar

liquids, like simple vegetable oils, can penetrate the threads with the dense silica coating. This leads to an oil uptake after placing them into an oil reservoir for 2 min and balancing them afterwards to calculate the oil amount.

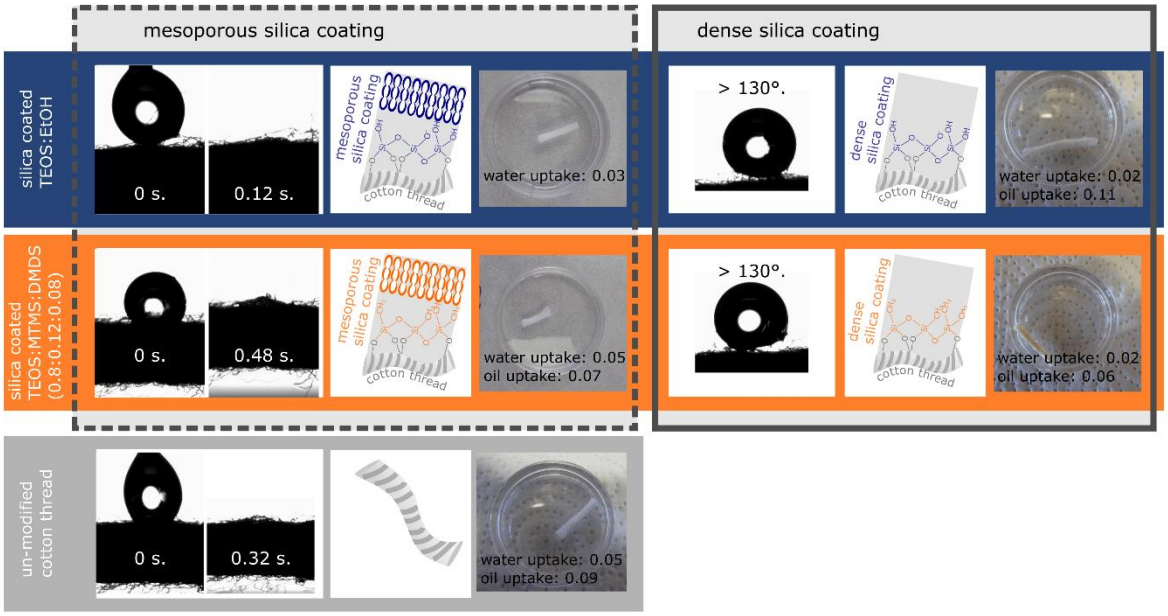


Figure S 7: Showing the static contact angle, the imbibition time and the water as well as the oil uptake after 2 min. of threads with different silica-based coatings.

Design of a set-up for dynamic imbibition experiments

To investigate the influence of the silica coatings on the dynamic imbibition properties of the cotton thread a new fluid imbibition set-up based on a fluid reservoir and two cuts in a distance of 5 cm for fastening the thread was designed. Due to the set-up design the modified thread is free floating which has the advantage that there are no additional forces influencing the imbibition process inside the thread next to the thread intrinsic capillary force.

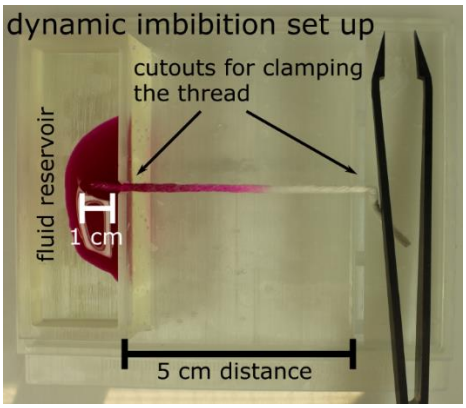


Figure S 8: Dynamic imbibition set-up to investigate the relation between thread coating and fluid transport velocity inside the cotton thread.

Knotting of the threads for polarity dependent fluid transport

Thread networks were obtained by knotting an unmodified, a mesoporous silica coated (with or without pore functionalization) and a dense silica coated together. To ensure an equal liquid distribution between the three threads starting from the unmodified thread which is the fluid supplier, they were knotted together with another unmodified thread with an overhand knot. The thread network is clamped into the imbibition set-up where the unmodified thread connects the network with the fluid reservoir (Figure S 9).

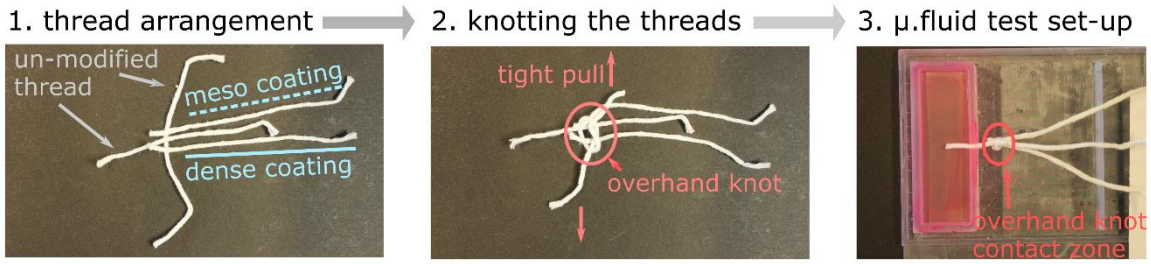


Figure S 9: Preparation steps of the thread network containing of two unmodified, a dense and mesoporous silica coated thread (step 1 and 2). Placement of the thread network inside the imbibition set-up for liquid guidance experiments.