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Fluid Flow Control in Cotton Threads with Mesoporous Silica Coatings

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Microfluidic devices are important, e.g. in the field of point of care diagnostics. They are of special importance, if they are fabricated out of cheap and renewable materials. Tackling complex separation or sensing problems profits from modular three-dimensional fluidic devices. Using cotton threads as renewable material allows the modular design of three-dimensional fluidic devices and networks. Here, fluidic threads with modular designed and tunable thread wettability are presented. The wettability is gradually adjusted from highly hydrophilic to hydrophobic. The thread wettability directly affects the fluid imbibition velocity as well as the distance, which the fluid imbibes into the thread. The wettability adjustment is based on a simple dense or mesoporous silica coating applied onto the cotton thread using sol-gel chemistry and evaporation induced self-assembly. In addition to wettability, the mesoporosity and the pore functionalization are used to tune the fluid velocity within the thread. Connecting different silica functionalized threads into one device by knotting them together, fluids can be guided through this network in a predicted manner, which allows a modular design of 3D microfluidic thread-based devices.

1. Introduction

Microfluidic devices are increasingly applied especially in the area of point of care diagnostic (PoC).[1] From the material perspective, paper or thread-based materials are integrated into microfluidic devices, because they show intrinsic microfluidic fluid transport due to their structure.[2] Paper as well as threads can be obtained from renewable resources and the production on a large

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scale is possible based on the already existing infrastructure, which makes them a cheap basic material.[2,3,4] To date, fluid imbibition and transport in paper are often controlled by the deposition of hydrophobic barriers with polymers or waxes.[3,5,6] The hydrophobic barriers create channels, and the fluid flow through the paper is tuned, for example, by the different channel width. This allows control of the fluid flow in the two dimensions of the paper sheet, which turned out as a limitation for more complex analytical systems.[3] With sudoku or origami paper-based microfluidic devices, which are combinations of printed hydrophobic barriers and multiple layers, three–dimensional (3D) devices were realized extending the potential of the common paper-based microfluidic devices.[7] Such sudoku or origami paper-based devices require a rather complex design with different sample application areas as well as detection zones, which need to get into contact resulting in systems that are complex to handle. Another option to create 3D fluidic devices, is the use of threads. Caused by the natural shape of the threads, no channels need to be created and the threads can easily be knotted to 3D networks.[2,8,9] Already in 2010, Reches et al. demonstrated the possibility of using threads as a matrix for biomedical assays.[10]

Seth et al. developed a microfluidic device containing cotton threads as fluid channels and nitrocellulose membranes as sensing areas. The threads were used to apply typical infection markers like IgG, H pylori, or Hepatitis A from the sample pad to the detection area containing anti-bodies in a controlled manner. With this set-up and based on the fluidic transport through the cotton threads, an immunochromatographic diagnosis of the mentioned reagents was established.[11] In the work of Tomimuro et al., a fluidic device based on cotton threads was designed for detecting different anti-bodies in a blood droplet. As a sensing mechanism, a bioluminescent reaction carried out at the cotton threads was implemented. This allows to evaluate the results easily and even camera-supported.[12] Ulum et al. show the application of cotton threads to separate blood cells from the blood plasma to detect the amount of Albumin in the next step, which is a biomarker for kidney or heart diseases.[13] Due to enzyme immobilization at the surface of cotton threads, Promphet et al. detected glucose and urea in sweat, which are markers for
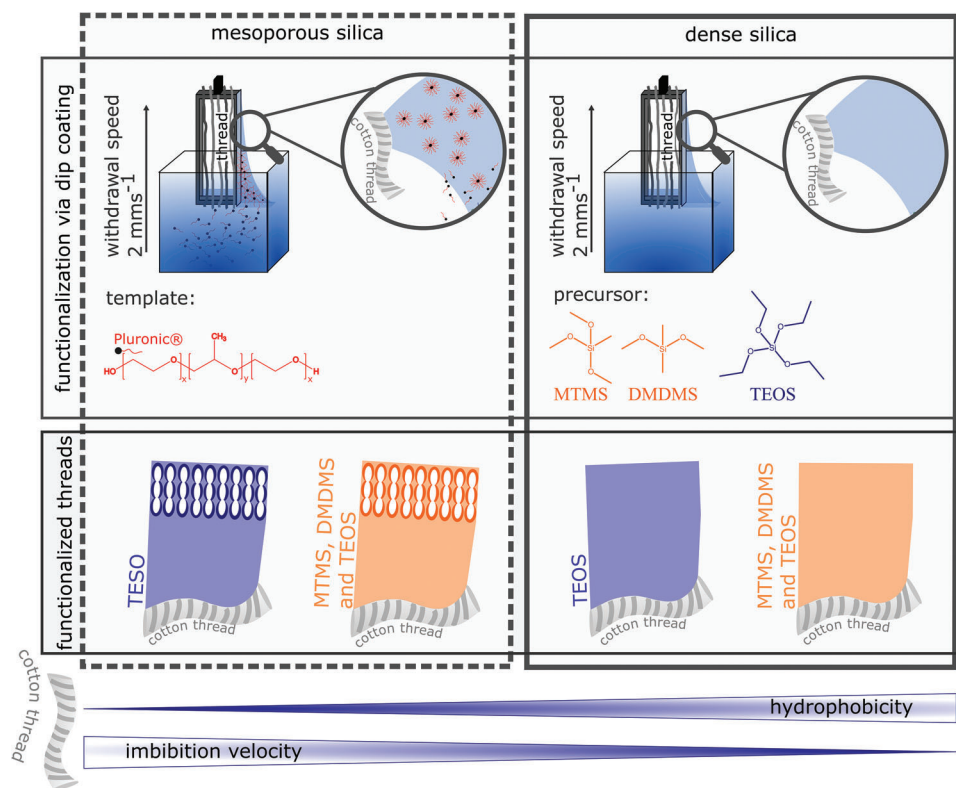
Figure 1. Schematic illustration of mesoporous and dense silica coatings with TEOS, MTMS, and DMDMS containing sol-gel solutions, and how the hydrophobicity as well as the imbibition velocity of the cotton thread is influenced by the silica coating.

diabetes or kidney failure.[14] They used a simple colorimetric system as read out unit, which provides an easy-to-use thread-based diagnostic device. However, all the microfluidic devices dealing with the detection of biomarkers with the corresponding antibodies which require a certain interaction time. Large inter-action time increases the sensitivity of the devices.[3,5,15] To in-crease the interaction time, the flow rate of the thread needs to be reduced, which was achieved by tuning of the thread intrin-sic structural and thus microfluidic properties. On the one hand, this can be realized with different kinds of knots as demonstrated by Safavieh et al.[16] and Ballerini et al..[9] On the other hand, this was achieved by surface modifications. To create a homogenous hydrophilic wettability along the cotton thread, various plasma treatments can be performed as have been reported by. Caschera et al.[17] Ya Dan et al. used a chitosan-based coating to maintain the hydrophilic character of cotton threads.[18] A reduction of the fluid transport velocity, which is especially of great importance to increase the sensitivity, was realized in the work of Choi et al. us-ing polysiloxane based coatings.[15] Due to the polysiloxane coat-ing, they were able to reduce the fluid flow of the cotton thread, which results in an optimum interaction between antigen and antibody and an improvement of the thread-based immunoas-say. Another approach to extend the interaction time between two compounds is to trap the analyte inside the test zone. This was demonstrated in the work of Wu et al. applying temperature-dependent wax patterns at the thread surface.[19] Complete water exclusion at cotton threads can be realized with a diamond-like

carbon coating, which was demonstrated by Caschera et al.[17] However, the strategies to tune the microfluidic character of the threads are limited to surface modifications. To the best of our knowledge, the control of the fluid transport velocity in cotton threads by the insertion of mesopores with polymer functional-ization has not been addressed in the literature so far.

Here, we present a strategy to tune the intrinsic wettability of cotton threads from highly hydrophilic to highly hydrophobic us-ing silica-based coatings. The silica-based coatings were gener-ated using sol-gel solutions containing the silica forming precur-sors tetraethoxysilane (TEOS) as well as methyltrimethoxysilane (MTMS) and dimethyldimethoxysilane (DMDMS). Thereby, the coatings were applied with and without a mesopore forming tem-plate. We report the conditions for mesopore formation at cotton threads during the coating procedure based on the evaporated in-duced self-assembly process (EISA), the impact of the mesopores on the fluid imbibition as well as a further wettability control due to pore functionalization. Based on the change of the wettability due to the silica coatings, the fluid imbibition velocity inside the threads can be accelerated as well as slowed down, or even com-plete exclusion of water can be obtained. While creating thread networks containing different functionalized threads, we are able to guide a liquid flow through the thread network with tunable fluid velocity and including fluid stop barriers. A controlled guid-ance of liquid based on different thread wettability is of great in-terest for more complex separation or detection processes in 3D thread-based devices.
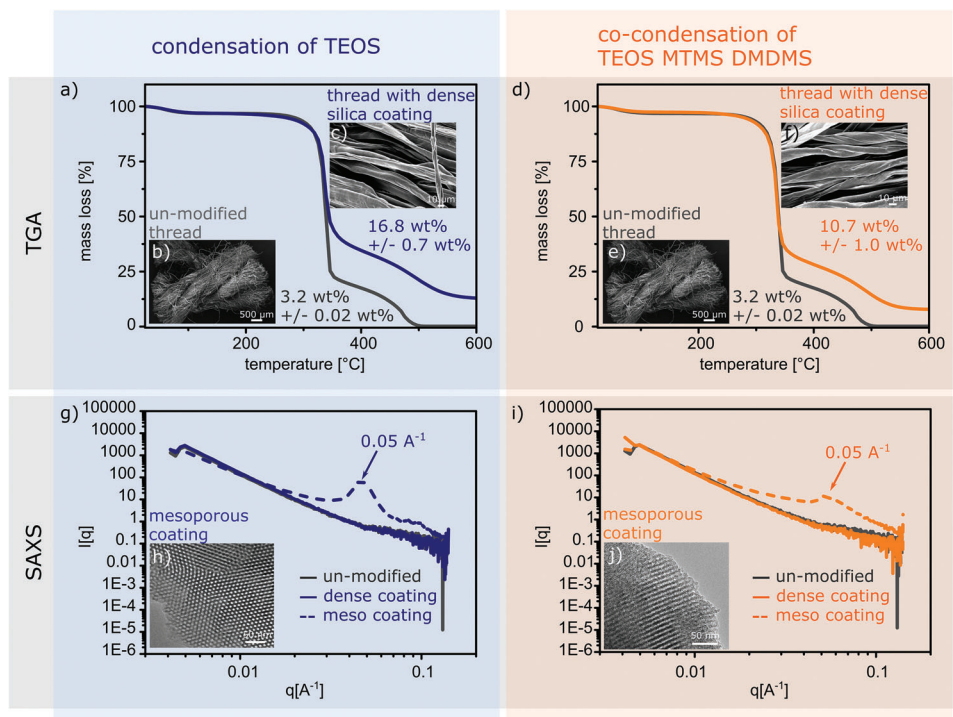
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Figure 2. TGA measurements of unmodified threads (grey plot), threads coated with sol-gel solution only containing TEOS (blue plot) and with co-condensed sol-gel solution (orange TGA plot) are shown in (a) and (d). b,e show SEM images of unmodified cotton thread. c) shows the SEM image of a cotton thread coated with a sol-gel solution containing only TEOS. f) SEM image of a thread coated with a sol-gel solution containing TEOS, MTMS, and DMDMS as precursor. g,i show SAXS measurements of an unmodified thread (grey plot), threads coated with dense silica coatings (blue and orange plots) and with mesoporous silica coatings (dashed blue and orange plots). h,j show TEM images of threads coated with mesoporous silica after the thermal removal of the thread. The sample size n for the TGA measurements is 3. The SEM, TEM, as well as SAXS measurements were performed on selected samples.

2. Results and Discussion

2.1. Surface Modification of Cotton Thread with Silica-Based Coatings

The intrinsic microfluidic properties of commercially available cotton threads were tuned based on a surface modification applying different silica coatings using sol-gel chemistry, EISA, and the dip-coating process. Dip coating was performed at a temperature of 25 ± 1 °C and a relative humidity of 50 ± 5 %. Functionalized threads were subsequently aged for one hour before they undergo a thermal post-treatment at a final temperature of 130 °C. The temperature treatment up to 130°C ensures a complete condensation of the silica precursor (Figure S1, Supporting Information). Cotton threads were modified either using silica (precursor TEOS) or using co-condensed silica containing the precursors MTMS and DMDMS in addition to TEOS. Thereby MTMS and DMDMS induce a hydrophobization of the coating. In addition to silica composition variation, both coatings were applied either with or without a mesopore forming template resulting in mesoporous or dense silica coatings. Depending on the applied silica coating, the hydrophobicity of the cotton thread can be tuned from highly hydrophilic to hydrophobic, and even water exclusion is possible. Consequently, the fluid imbibition velocity of water or other fluids within the thread can be adjusted (**Figure 1**).

The amount of silica coated on the threads was determined using thermogravimetric analysis (TGA). For unmodified cotton threads, a residue of 3.2 ± 0.02 wt.% remains after a temperature treatment up to 600 °C (**Figure 2**a,b grey). After coating dense silica, a coating amount of 13.6 ± 0.7 wt.% is deposited onto the cotton thread (Figure 2a blue). With dense silica coatings containing MTMS and DMDMS in addition to TEOS as the silica precursor, a silica residue of 7.5 ± 0.1 wt.% is obtained (Figure 2d orange). This silica coating amount of the coatings containing MTMS, DMDMS, and TEOS is 6 wt.% lower as compared to the dense silica coating amount, which indicates the calcination of the organic groups from MTMS and DMDMS during thermogravimetric analysis. Comparing the SEM image, no structural differences between unmodified cotton threads (Figure 2b,e; Figure S5, Supporting Information) and cotton threads with dense silica coating (Figure 2c with TEOS and f with TEOS, MTMS, and DMDS as precursor) are observed. This is in agreement with the relatively low coating amount of 13.6 ± 0.7 wt.% and 7.5 ± 0.1 wt.%, which seems to be homogenously distributed along the cotton thread. Small angle X-ray scattering (SAXS) measurements of unmodified as well as dense silica coated cotton threads show identical results (Figure 2g,i), which further support the absence of significant structural changes. Neither the SAXS measurements for unmodified cotton threads (Figure 2g grey, Figure 2i grey) nor the corresponding dense silica coated cotton threads (Figure 2g blue, Figure 2i orange) display diffraction peaks ruling out the
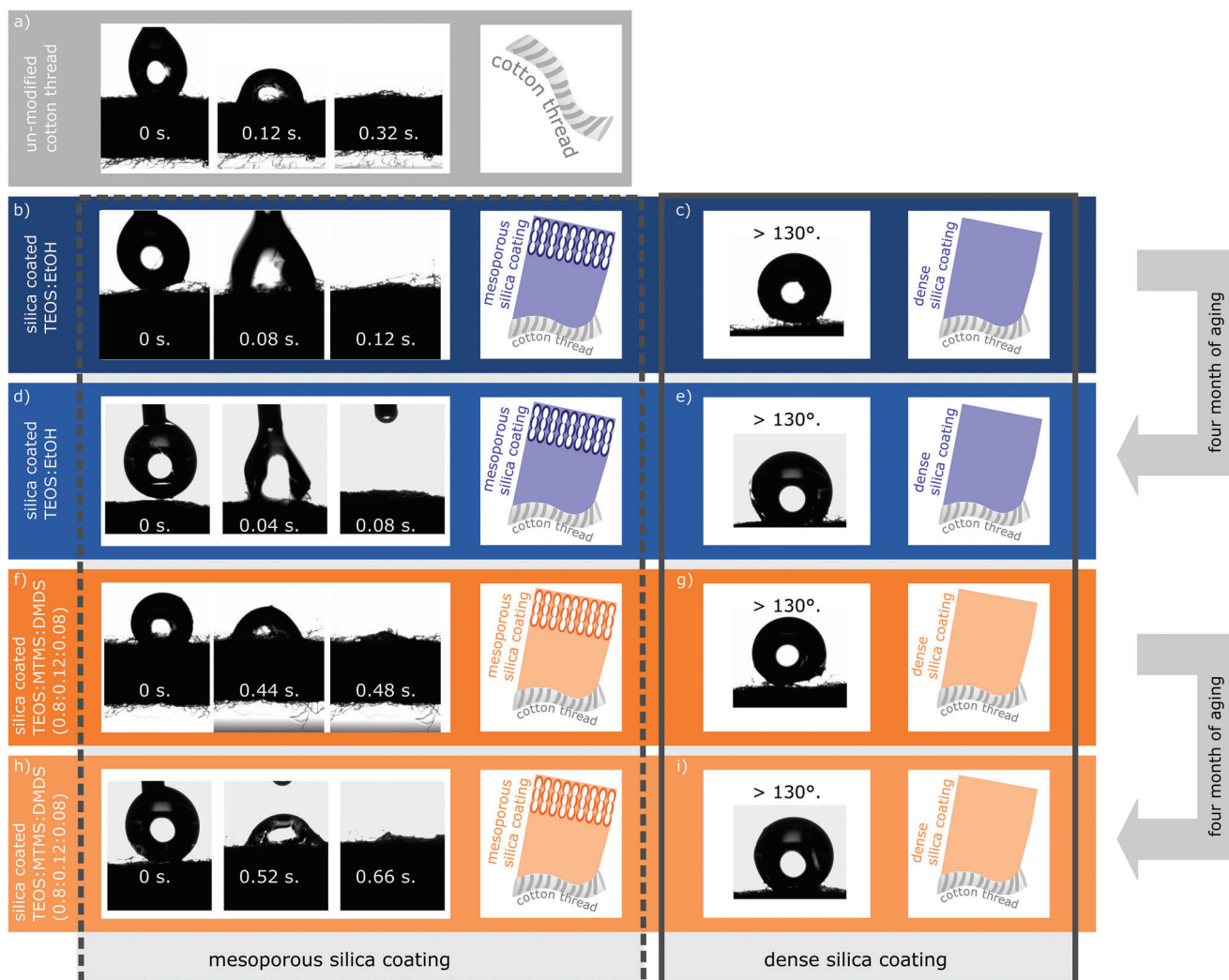
Figure 3. a,b,f show the imbibition process of a 2 µL water droplet into an unmodified a), with a freshly mesoporous silica coated b) and a freshly mesoporous silica coated thread with in situ pore functionalization f). d,h show the imbibition process of mesoporous silica coated d) and mesoporous silica coated threads with in situ pore functionalization h) they aged for 4-month. c,g show the static contact angle for threads coated with a dense sol-gel solution containing only TEOS c) and a co-condensed sol-gel solution e). The hydrophobic character remains after the samples aged for 4-months, which is shown in (e) and (i). At least 3 samples were analyzed using static contact angle measurements. CA was measured at 3 to 5 different spots at the thread surface to ensure a uniform wettability due to the silica coating (n = 3–5).

existence of translational order. Contrary, in case of mesoporous silica coated cotton threads, a broad Bragg peak is indicating ordered mesopore formation (Figure 2g dashed blue and Figure 2i orange dashed). For both mesoporous silica coatings (TEOS and TEOS, MTMS, DMDMS), a Bragg peak at 0.05 nm^{-1} is obtained, whereby the intensity as well as shape of the peak is more pronounced for the unfunctionalized mesoporous silica coating containing only TEOS. These Bragg peaks indicate scattering centers in mesoporous size range, which are arranged in a regular distance of ≈12.3 nm. The structural information obtained by SAXS is in accordance with the TEM results. In the TEM images of the unfunctionalized mesoporous silica coating (Figure 2h; Figure S6, Supporting Information) as well as for the mesoporous silica coating containing MTMS and DMDMS (Figure 2j, Figure S6, Supporting Information), mesopores are visible in the size of 6 ± 0.5 nm. The more defined, sharper, and intense Bragg peak

for the unfunctionalized mesoporous silica coating implies a larger number of mesopores and a higher orientation of the structural domains to each other as compared to the mesoporous silica coating containing TEOS, MTMS, and DMDMS. This is consistent with TGA results showing a slightly larger coating amount for silica coated threads. An unfunctionalized mesoporous silica coating amount of 13.0 ± 0.5 wt.% is deposited at the threads. Whereas with the TEOS, MTMS, and DMDMS co-condensed sol-gel solution, a mesoporous silica amount of 10.3 ± 0.3 wt.% is deposited. In the case of threads coated with TEOS, MTMS, and DMDMS, the broad Bragg diffraction peaks indicate that although the system displays crystalline order, the size of the domains is small as reflected by peak broadening. Moreover, inspection of the diffraction image recorded by the detector indicates that the crystalline domains do not display noticeable preferential orientation. The differences in the domain size are supported by
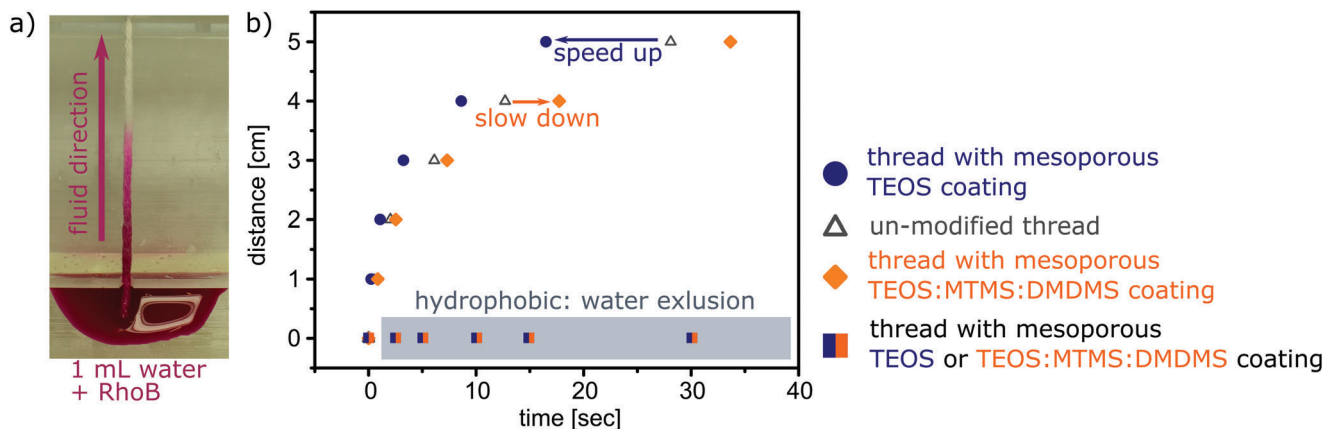
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Figure 4. a) shows the set-up for the dynamic imbibition experiments using water dyed with Rhodamine B. The plot in (b) shows the time that the fluid front needs to pass a certain distance. Dynamic imbibition experiments were performed at 5 samples per silica functionalization. The mean value was used for creating the imbibition distance related to the time plot ($n = 5$).

the TEM images. In the TEM image of the thread sample coated with the unfunctionalized mesoporous silica coating, it is clearly observable that pores are arranged in a hexagonal structure inside their domains, and the domains as well show an orientation to each other (Figure 2h). The pore orientation inside the domains and the lower domain-domain orientation are in accordance with

the TEM image for the thread coated with the MTMS, DMDMS, and TEOS containing mesoporous silica coating (Figure 2j).

2.2. Influence of Cotton Thread Surface Modification with Silica-Coatings on the Wettability as well as on the Fluid Transport

To investigate the influence of the silica coatings on the wettability of the cotton threads, static water contact angles were recorded. Unmodified cotton threads are highly hydrophilic as it is shown in **Figure 3**a. A 2 µL water droplet imbibes into the thread within 0.32 s after the deposition at the thread surface. This hydrophilicity is accompanied by an intrinsic microfluidic water uptake, which allows the transport of fluids in these threads. For a controlled fluid transport, especially with regard to thread-based assays,[10] the wettability, and with this the fluid transport within the threads, needs to be tuned in a controlled manner. When applying mesoporous silica coatings, the cotton threads remain hydrophilic (Figure 3b,d), and the water droplet imbibes into the thread directly after the droplet deposition. In cotton threads with an unfunctionalized mesoporous silica coating, the 2 µL water droplet completely imbibes within 0.12 s (Figure 3a). Compared to the unmodified thread, the imbibition is accelerated due to the introduction of unfunctionalized silica mesopores, which is indicating an increased capillary force. When applying a mesoporous silica coating containing MTMS and DMDMS, the fluid imbibition velocity is reduced as compared to the unmodified cotton thread as well as compared to the unfunctionalized mesoporous silica coating. After the droplet deposition, the water droplet penetrates slowly into the thread (0.44 s). Step by step, the static contact angle decreases before the droplet completely enters the thread after ≈0.48 s (Figure 3a,d). This reduction of imbibition speed is caused by the presence of nonpolar MTMS and DMDMS within the mesoporous silica coating which renders this coating more hydrophobic. Applying dense silica coating with a minimum coating amount of 4 wt.% (Figure S4, Supporting Information) to the thread, a static contact angle above 130 ° is obtained which results in water exclusion (Figure 3c,e). The hydrophilic as well as hydrophobic character of
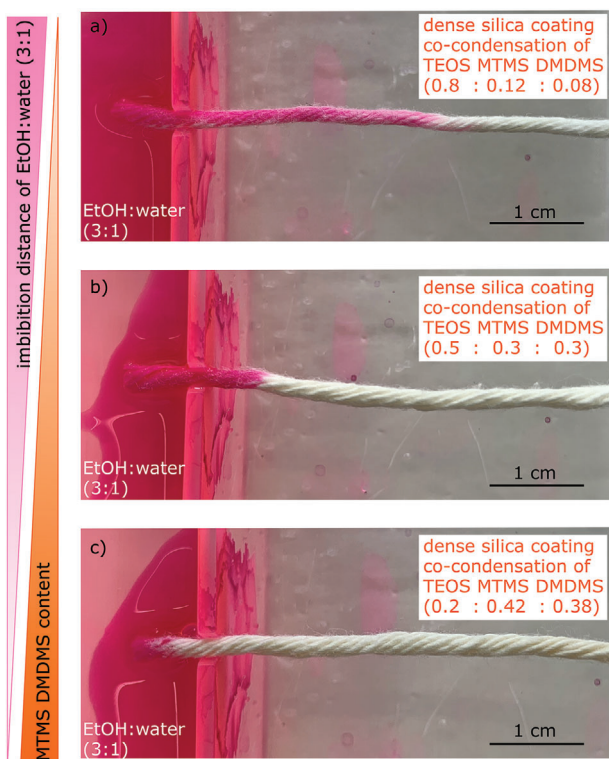

Figure 5. show the imbibition and the imbibition distance after 1 min of a EtOH:water mixture (3:1) in cotton threads coated with dense silica containing TEOS, MTMS, and DMDMS and three different ratios. The imbibition distance of the fluid mixture EtOH:water is 3:1 after 1 min. were measured for 3 samples per sample type ($n = 3$).
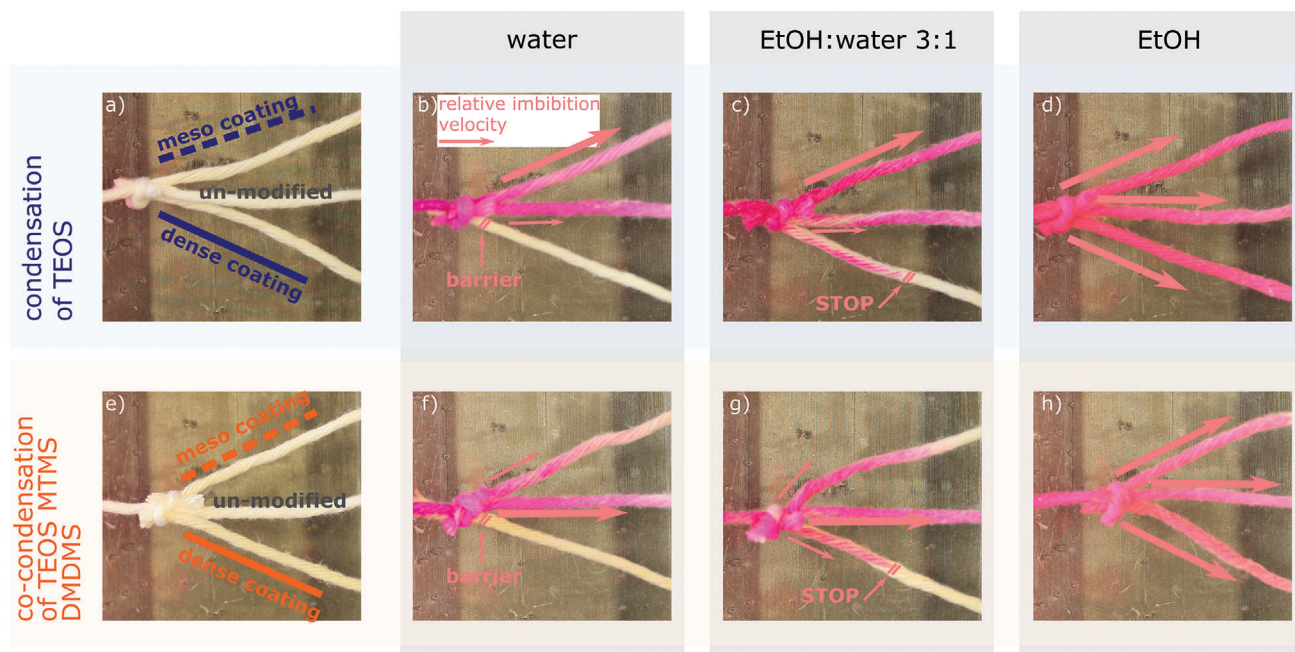
Figure 6. a,e) show the composition and connection of the investigated thread networks. The network consists of an unmodified thread, threads with a mesoporous silica and dense silica coating are connected with an overhand knot. The thread network in (e) consists of an unmodified thread, a thread with a methyl-group functionalized mesoporous silica coating, and a dense silica coating. b,f) are representing the imbibition and the fluid distribution inside the thread network when using water as polar fluid. c,g) show the change in the fluid distribution inside the network when using a liquid mixture of ethanol and water in a ratio of 3:1. Due to the solvent mixture the liquid is less polar than "pure" water. d,h) show the equal fluid distribution inside the three threads based on the lower polarity of ethanol compared to the two other liquids. Every network liquid combination was tested three times ($n = 3$).

the modified cotton threads is still observed even after 4-month of storage which is shown in Figure 3c,e,g,i.

To investigate the time dependent fluid imbibition velocity along cotton threads and how it is influenced by the different silica coatings, the threads were clamped into a holder with a distance of 5 cm between the two clamps. On the one side of the holder, a fluid reservoir is located allowing one end of the thread to be in contact with 1 mL of liquid (**Figure 4**a). The time dependent movement of the fluid front was recorded (Figure 4b). Unmodified cotton threads show a fast imbibition in the range of short distance close to the imbibition starting point. With increasing distance, the imbibition velocity slows down (Figure 4b grey triangles). As expected from the static contact angle measurements, threads with an unfunctionalized mesoporous silica coating (Figure 4b blue dots) show a faster water imbibition velocity than unmodified cotton threads (Figure 4b grey triangles), which is ascribed to the additional capillary force due to the mesopore network of the mesoporous silica coating. A reduction of the imbibition velocity as compared to the unmodified cotton threads is observed for threads with a mesoporous silica coating containing MTMS and DMDS (Figure 4b blue orange square) due to the more hydrophobic character of the mesoporous silica coating. Samples with a dense silica coating show a static contact angle above 130° and hence do not show any water imbibition. This effect of dense silica coatings is in accordance with previous results for dense silica coatings on paper, and it is ascribed to a pinning effect and the suppression of fiber swelling due to the dense silica coating.[20]

Besides water imbibition fluids with lower polarity are still capable of imbibing into the dense silica coated, hydrophobic cotton threads (**Figure 5**). Nevertheless, co-condensation of nonpolar methoxy groups can be used to precisely tune the imbibition distance which then can be utilized, for example, as a sensor tool. Upon variation of the nonpolar methoxy group content in the dense silica coating by varying the TEOS, MTMS, and DMDMS ratio, cotton threads with a hydrophobic character are obtained. When analyzing ethanol (EtOH) : water = 3:1 imbibition for decreasing TEOS content from 80 mol% – 20 mol% (Figure 5) the distance of fluid imbibition after 1 min is reduced from 3 to 0.5 cm to no imbibition. This shows the possibility to precisely adjust fluid imbibition speed and distance not only for water but as well for more nonpolar fluids and fluid mixtures by adjusting the silica composition.

Hence, the chemical composition of the coating together with the nanoscale porous structure affect the wettability and the time dependent imbibition velocity of the cotton thread. Both parameters allow gradual tuning of the fluid imbibition along the cotton thread. While knotting threads together to a network, sections with different time dependent imbibition velocities can be combined, which enables a targeted guidance of liquids. Highly polar liquids, such as water, can pass through threads that are hydrophilic. This is the case for unmodified threads and threads with a mesoporous silica coating. With an increase of the thread hydrophobicity, which can be obtained with a mesoporous silica coating containing TEOS, MTMS, and DMDMS, the polar liquids get decelerated until the imbibition stops. Polar liquids are not

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able to enter threads with a dense silica coating being hydrophobic with a static contact angle above 130°. Thus, these dense silica coated threads represent a liquid barrier for hydrophilic liquids such as water. In contrast, liquid imbibition into threads with a dense silica coating can be observed for less polar liquids such as ethanol or ethanol water mixtures. Here, the relative imbibition velocity is slower as for the unmodified threads or in the thread with a mesoporous silica coating, which leads to a stop of the imbibition after a certain distance.

The properties of the silica coatings on the fluid imbibition in 3D microfluidic thread devices were investigated with three liquids having different polarities (water > EtOH : water 3:1 ratio > EtOH), which were applied to thread networks consisting of three different functionalized threads connected via a knot (see Figure S9, Supporting Information). The first thread network consists of an unmodified cotton thread, which also serves as connection between the fluid reservoir and the thread network, an unfunctionalized mesoporous silica coated (highly hydrophilic, CA < 75°) and dense silica coated (highly hydrophobic, CA > 130°) thread (**Figure 6**a–d). The three threads were connected using an overhand knot, which is the starting point for the liquid distribution inside the thread network. When bringing the network into contact with water (polar liquid), the water imbibes into the unmodified thread and gets relayed at the knot to the thread with the unfunctionalized mesoporous silica coating. Based on the porous silica coating, the imbibition velocity is faster inside the unfunctionalized mesoporous silica coated thread (upper thread Figure 6b) and thus more liquid is transported via this thread. Behind the knotting point, the fluid imbibition continues in the unmodified cotton thread. Due to the modification, a higher relative imbibition velocity inside the thread network is obtained with the unfunctionalized mesoporous coating. To visualize the different relative imbibition velocities inside the thread network, long and bold arrows representing a fast relative imbibition velocity and short, thin arrows for a slow relative imbibition velocity are placed beside the threads in Figure 6. Due to its hydrophobic character, the water does not imbibe into the thread with the dense silica coating and thus the thread acts as a water stop barrier in the thread network (Figure 6b). Decreasing the polarity of the liquid by using EtOH : water mixtures with a ratio of 3:1 again allows fluid imbibition into the dense silica coated thread. Nevertheless, the relative imbibition velocity decreases as compared to unmodified or mesoporous silica modified threads, and the liquid stops passing the thread after a certain distance behind the knot (Figure 6c). Imbibition of the ethanol water mixture inside the unfunctionalized mesoporous silica coated cotton thread as well as in the unmodified thread occurs in a comparable manner as observed for pure water. When using ethanol (Figure 6d), it penetrates all three threads in the same fashion with a comparable relative fluid imbibition velocity and the liquid gets distributed homogenously inside the thread network (Figure 6d).

To obtain a thread network with a deceleration in the relative imbibition velocities compared to an unmodified thread network, a second thread network consisting of an unmodified thread for the liquid supply and a thread with a mesoporous coating as well as a thread modified with a dense silica coating containing TEOS, MTMS, and DMDMS (Figure 6e–h) was constructed. When applying water as a polar liquid into the network, the liquid dis-

tributes starting from the knotting point into the thread with the MTMS and DMDMS containing mesoporous coating and in the unmodified thread. Thereby the relative imbibition velocity inside the MTMS and DMDMS containing mesoporous coated thread is slower than for the unmodified thread as well as slower as compared to the unfunctionalized mesoporous silica thread discussed above (Figure 4a). Thus, less liquid is transported in the MTMS and DMDMS containing mesoporous coated thread. As expected, no imbibition into the dense silica coated thread containing MTMS and DMDMS was observed (Figure 6f). Decreasing the liquid polarity by using a 3:1 ethanol water mixture, the liquid can enter the thread with the dense silica coating containing MTMS and DMDMS. Again, the relative imbibition velocity is lower than for unmodified threads and in contrast to the observation for dense silica without MTMS and DMDMS. The fluid front stops after a specific distance after the knot. Thereby, the fluid stop occurs at a shorter distance with respect to the imbibition front as observed for dense silica coated cotton threads. The relative imbibition velocity is slower in the mesoporous silica coated thread containing MTMS and DMDMS than in the unmodified thread (Figure 6g). Bringing the thread network into contact with the less polar liquid ethanol, the liquid is distributed equally inside the thread network with the same relative imbibition velocity independently of the thread functionalization (Figure 6h).

3. Conclusion

Using mesoporous and dense silica coatings with adapted molecular composition, the intrinsic wettability and fluid imbibition velocity of cotton threads were tuned from highly hydrophilic to hydrophobic. Dense silica coated threads with a minimum silica coating amount of 4 wt.% prevent water imbibition and were used as a water stop barrier. With the introduction of mesopores into the coating, the threads remain hydrophilic even if nonpolar silica precursors such as MTMS or DMDMS are included into the coating. The unfunctionalized mesoporous silica coating shows an acceleration of the fluid imbibition velocity ascribed to an additional capillary force due to the introduced mesopore structure. In contrast, the mesoporous silica coating containing nonpolar MTMS and DMDMS shows a reduced fluid imbibition velocity. Upon connecting differently coated threads into a network, the fluid flow of water, of water ethanol mixtures as well as of pure ethanol can be guided through this thread network in a defined manner. Dense silica coatings represent a stop barrier for water, whereas ethanol-water mixtures show a silica composition dependent stop distance. Thus, barriers as well as imbibition speed accelerator and decelerating paths can be combined. This is of relevance for separation as well as more complex detection processes in a simple 3D microfluidic thread-based approach.

4. Experimental Section

Reagents: All chemicals and solvents were purchased from Merck and used as received.

Threads: Commercially available cotton thread of the brand Cotton Universal, containing 100% cotton (Art-Nr 300 005, Farb-Nr 038).

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Dense and Mesoporous Sol-Gel Solutions: To prepare a mesoporous silica coating at the thread surface, a sol-gel solution containing TEOS as precursor and the mesopore forming template Pluronic F127 was prepared with the following molar ratios: 1 TEOS : 20 EtOH : 0.05 F127 : 5 H2O : 0.01 HCl. A dense silica coating was realized with the same composition but in the absence of the template PluronicF127. Before use, the freshly prepared sol-gel solution was stirred for 24 h at room temperature. The mesoporous silica coating containing MTMS and DMDMS was realized via co-condensation. Therefore, a sol-gel solution containing the precursor TEOS, MTMS, and DMDMS as well as Pluronic F127 was prepared with the following molar ratios: 0.8/0.5/0.2 TEOS : 0.2/0.3/0.42 MTMS : 0.08/0.2/0.38 DMDMS : 40 EtOH : 0.0075 F127 : 10 H2O : 0.028 HCl. To create a dense silica coating containing these three precursors, a sol-gel solution was prepared with the same ratios as described above but without the micelle forming Pluronic F127. Also, the sol-gel solution for the co-condensation of the three-precursors was stirred at room temperature for 24 h before use.

Thread Functionalization: For the dip coating procedure cotton threads with a length of 6 cm were clamped into a holder which were dipped into the sol-gel solution and withdrawn with a withdrawal speed of 2 mms^{-1}. The dip-coating procedure was performed at a relative humidity of 50 ± 5 % and a temperature of 25 ± 1 °C. Freshly modified cotton threads aged for 1 h under the same humidity and temperature, before they undergo a thermal post-treatment. The first treatment was carried out at 60 °C for 1 h before the temperature was increased to 130 °C in 10 min which was kept again for 1 h. To remove template in the mesoporous silica coating, the template was extracted in a 1 M acidic ethanol bath for 3 days.

Thermogravimetric Analysis (TGA): Thermogravimetric measurements were performed using a TGA 1 instrument from Mettler Toledo. The silica coated cotton threads were placed in a 100 μL Al crucible and the following temperature program was applied for the controlled combustion of the organic part: The hybrid material was heated from 25 to 600 °C at a rate of 10 °C min^{-1} under constant air flow of 30 mLmin^{-1}. The maximum temperature of 600 °C was maintained for 10 min. For the data evaluation the corresponding program Star1 was used.

Scanning Electron Microscopy (SEM): SEM images were obtained by using a Zeiss ECO 10 scanning microscope at high vacuum and an acceleration voltage of 10 kV. To create a conductive coating a 10 nm thick platinum(80)/palladium(20) (from ESG Edelmetall-Service Rheinstetten; charge number IN0145660) layer was applied using a sputter coater (Cressington 208HR).

Transmission Electron Microscopy (TEM): TEM images were recorded on JEOL JEM 2100F microscope with a maximum resolution of 2.2 Å at an acceleration voltage of 200 kV. TEM samples were prepared by drop-casting ≈5 μL of the silica film dispersion in ethanol (sonicated for 5 min beforehand) on carbon-coated copper grids (3.05 mm, 200 mesh size) followed by air-drying overnight.

Small Angle X-Ray Scattering (SAXS): SAXS experiments were performed in a XEUSS 1.0 SAXS setup (XENOCs, Grenoble, France). Monochromatic X-rays (λ = 0.15419 nm) were produced with a GENIX 3D micro-focus tube. The incoming X-ray beam was collimated to have a size at sample position of 0.5 × 0.5 mm^2. Scattered photons were detected using a PILATUS 100K detector placed at D = 2500 mm sample to detector distance (calibrated using Silver Behenate as standard).

Static Contact Angle: The contact angle measurement was carried out using a Model TBU90E from DataPhysics Instruments GmbH with the corresponding software. For the macroscopic static contact angle measurements and the analysis of the droplet imbibition velocity, a water droplet with a volume of 2 μL with a dosing rate of 1 μLs^{-1} was applied to the thread surface. The imbibition process was recorded, whereby the time of the droplet imbibition was extracted from the recorded video.

Dynamic Fluid Imbibition: To investigate the dynamic fluid imbibition into silica modified threads, the samples were clamped into a newly designed imbibition set-up (Figure S7, Supporting Information). 1 cm of the thread end was placed into a fluid reservoir into which 1 mL of rhodamine-stained distilled water was added with a pipette. The imbibition along the thread was recorded with a Canon EOS 600D. The evaluation of the recorded videos with regard to the imbibition distance and time depen-

dent imbibition distance was performed manually using the program Fiji after the conversion from avi to raw format using the free program ffmpeg.

Thread Networks: Thread networks consisting of differently functionalized threads were obtained by knotting the threads together using an overhand knot. The thread network was clamped into a 3D printed imbibition set-up. The liquid supply was established through an unmodified thread providing the connection between the thread network and the fluid reservoir. 1 mL of polar (water), intermediated polar (EtOH : water with a ratio of 3 : 1) and less polar (EtOH) liquid stained with the dye rhodamine B were placed into the liquid reservoir.

Data Reproduction: The obtained analytical data for example of the TGA, contact angle measurements, and fluid imbibition experiments were directly used for the evaluation without any further data manipulation. From this original data analysis as described in the corresponding characterization experimental section each mean value and error bar given in the manuscript is based on five to ten reproduction experiments in material fabrication and subsequent characterization. SAXS measurements, SEM, and TEM images have been performed on selected samples at different spots at the surface.

In all the figures and tables, the main value and the standard deviation are indicated which were calculated using the following formula using excel or origin as software.

Mean Value:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \tag{1}$$

x: experimental data
n: number of experiments that were performed with the same parameters

Standard Deviation:

$$\sigma(x) = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2} \tag{2}$$

σ: standard deviation
x: experimental data
n: number of experiments that were performed with the same parameters

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

[1] S. Sharma, J. Zapatero-Rodríguez, P. Estrela, R. O'Kennedy, *Biosensors (Basel).* **2015**, *3*, 577.

[2] W. Tan, E. Powles, L. Zhang, W. Shen, *Sens. Actuators, B* **2021**, *334*, 129670.

[3] E. Noviana, T. Ozer, C. S. Carrell, J. S. Link, C. McMahon, I. Jang, C. S. Henry, *Chem. Rev.* **2021**, *121*, 11835.

[4] R. S. P. Malon, L. Y. Heng, *E. P, Córcoles Reviews in Analytical Chemistry* **2017**, *36*, 20160018.

[5] S. Nishat, A. T. Jafry, A. W. Martinez, F. R. Awan, *Sens. Actuators, B* **2021**, *336*, 129681.

[6] L. M. Hillscher, V. J. Liebich, O. Avrutina, M. Biesalski, H. Kolmar, *ChemTexts* **2021**, *2*, 14.

[7] a) F. Arduini, S. Cinti, V. Caratelli, L. Amendola, G. Palleschi, D. Moscone, *Biosens. Bioelectron.* **2019**, *126*, 346; b) C.-A. Chen, W.-S. Yeh, T.-T. Tsai, Y.-D. Li, C.-F. Chen, *Lab Chip* **2019**, *4*, 598; c) X. Li, X. Liu,

[8] D. Agustini, F. R. Caetano, R. F. Quero, J. A. Fracassi da Silva, M. F. Bergamini, L. H. Marcolino-Junior, D. P. de Jesus, *Anal Methods* **2021**, *41*, 4830.

[9] D. R. Ballerini, X. Li, W. Shen, *Biomicrofluidics* **2011**, *1*, 14105.

[10] M. Reches, K. A. Mirica, R. Dasgupta, M. D. Dickey, M. J. Butte, G. M. Whitesides, *ACS Appl. Mater. Interfaces* **2010**, *6*, 1722.

[11] M. Seth, D. Mdetele, J. Buza, Microfluidics and Nanofluidics **2018**, *22*, 45.

[12] K. Tomimuro, K. Tenda, Y. Ni, Y. Hiruta, M. Merkx, D. Citterio, *ACS Sens.* **2020**, *6*, 1786.

[13] M. F. Ulum, L. Maylina, D. Noviana, D. H. Wicaksono, *Lab Chip* **2016**, *8*, 1492.

[14] P. Punnoy, P. Preechakasedkit, C. Aumnate, N. Rodthongkum, P. Potiyaraj, N. Ruecha, *Mater. Lett.* **2021**, *299*, 130076.

[15] J. R. Choi, A. Nilghaz, L. Chen, K. C. Chou, X. Lu, *Sens. Actuators, B* **2018**, *260*, 1043.

[16] R. Safavieh, G. Z. Zhou, D. Juncker, *Lab Chip* **2011**, *15*, 2618.

[17] D. Caschera, A. Mezzi, L. Cerri, T. de Caro, C. Riccucci, G. M. Ingo, G. Padeletti, M. Biasiucci, G. Gigli, B. Cortese, *Cellulose* **2014**, *1*, 741.

[18] Y. D. Li, W. Y. Li, H. H. Chai, C. Fang, Y. J. Kang, C. M. Li, L. Yu, *Cellulose* **2018**, *8*, 4831.

[19] T. Wu, T. Xu, L.-P. Xu, Y. Huang, W. Shi, Y. Wen, X. Zhang, *Biosens. Bioelectron.* **2016**, *86*, 951.

[20] a) M. Nau, N. Herzog, J. Schmidt, T. Meckel, A. Andrieu-Brunsen, M. Biesalski, *Adv. Mater. Interfaces.* **2019**, *18*, 1900892; b) J. J. Mikolei, L. Neuenfeld, S. Paech, M. Langhans, M. Biesalski, T. Meckel, A. Andrieu-Brunsen, *Adv. Mater. Interfaces.* **2022**, *19*, 2200064.

[21] X. Li, J. Tian, W. Shen, *ACS Appl. Mater. Interfaces* **2010**, *1*, 1.

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