**Supporting Information**

**Single-Fibre Coating and Additive Manufacturing of Multifunctional Papers**

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**Paper fabrication equipment**

Paper fabrication was performed by using fibre deposition or the fibre printing technique. For fibre deposition, stir-coated fibres were poured onto the metal wire of a miniaturized paper sheet former, and a vacuum was applied (**Figure S 1,** Upper part). This process resulted in the formation of a paper sheet on the metal wire. After the complete removal of the sol-gel solution, the formed paper sheets were transferred onto a glass substrate, and a thermal posttreatment was performed as described in the experimental section. With the fibre deposition paper fabrication technique, paper with asymmetric wettability along the paper sheet cross section can be attained by layerwise fibre deposition, which allows the control of a (step) gradient fibre composition along the paper cross section.

Paper sheets with wettability patterns in the paper plane can be generated via fibre printing (**Figure S 1**, Lower part). Therefore, fibres with or without functionalization are applied onto a metal wire using a nozzle. The sol-gel solution is directly removed from the deposited fibres by applying a vacuum. A motor is used to move the nozzle over the wire. The motor and thus the nozzle are controlled by software, which allows the precise design of fibre patterns.

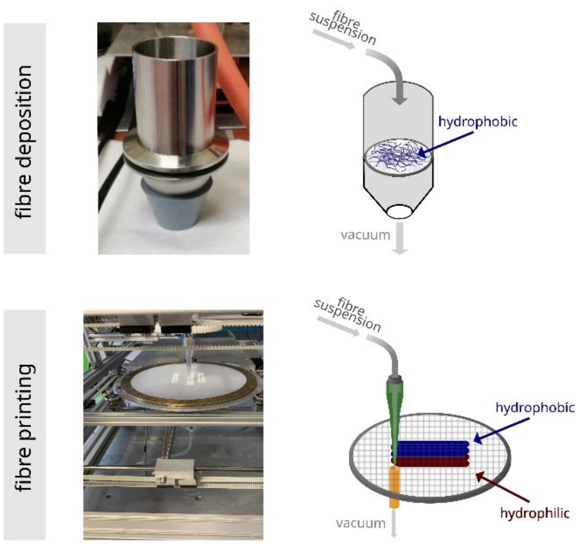

**Figure S 1** Upper part: Paper production by using a miniaturized paper sheet former. Lower part: Attainment of papers with wettability patterns by using the fibre printing technique.

## Comparison of the functionalization methods

**Table S 1:** Comparison of the stir coating process with subsequent paper production to inkjet and wax printing functionalization in the fields of functionalization, coating solution, functionalization in paper dimensions, pattern shape, resolution, and biocompatibility.

| | fibre printing[1-7] | fibre deposition[4-7] | Inkjet/wax printing[8-12] |
|---|---|---|---|
| functionalization of | individual fibre | individual fibre | paper sheet |
| coating solution | sol-gel solution | sol-gel solution | e.g. poly(dimethylsiloxanen), silica nanoparticles different waxes |
| functionalization in the paper dimension | paper plane | paper cross-section | paper plane |
| pattern shape | paper areas | asymmetric wettability | barriers |
| resolution | | millimetre range | 600 µm |
| biocompatibility | yes | yes | upon the used ink/waxes |

## Miniaturized paper sheet former

Paper manufacturing via fibre deposition was performed following the sheet-forming process described in ISO 5269/2, DIN 54358, and Zellcheming Merkblatt V/8/75. To miniaturize the process, a sheet-forming setup consisting of 7 different parts was designed. The bottom part consists of a stainless-steel coherent piece, which fits into a standard vacuum flask, whereby vacuum can be applied (**Figure S 2.**1 upper line). A 3D-printed inlay made of a hydrophobic polymer, which hinders the direct dehydration of the fibre solution before applying vacuum, can be precisely inserted into the bottom part (Figure S 2.2 upper line). The metal wire is placed on top of the inlet, on which the fibres form the paper sheet (Figure S 2.3 upper line). A sealing ring was placed between the bottom and top parts of the miniaturized sheet former (Figure S 2.4 upper part). The lower and top parts are connected with a sleeve (Figure S 2.1 and Figure S 2.2 lower line). Due to the top part, 50 mL of fibre suspension can be used for the sheet forming process.

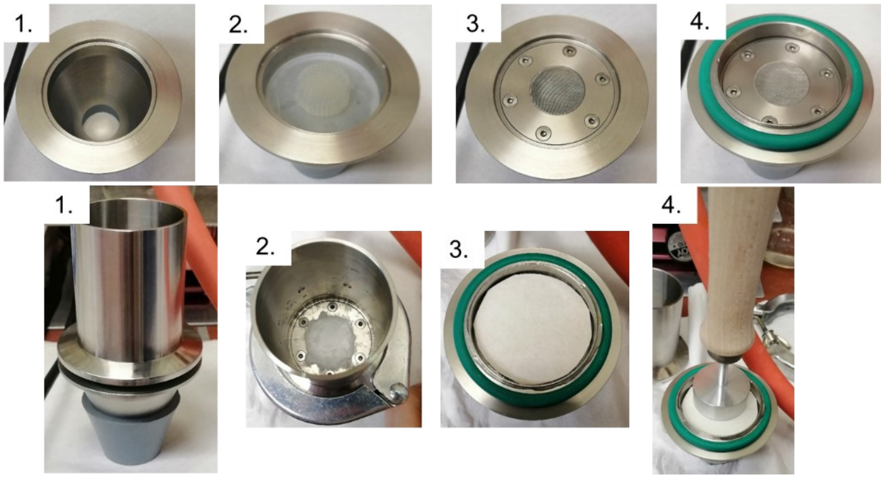


**Figure S 2:** Setup with the different parts of a miniaturized sheet former based on the Rapid Köthen sheet former.

## Microscopic analysis of papers made of silica-coated papers

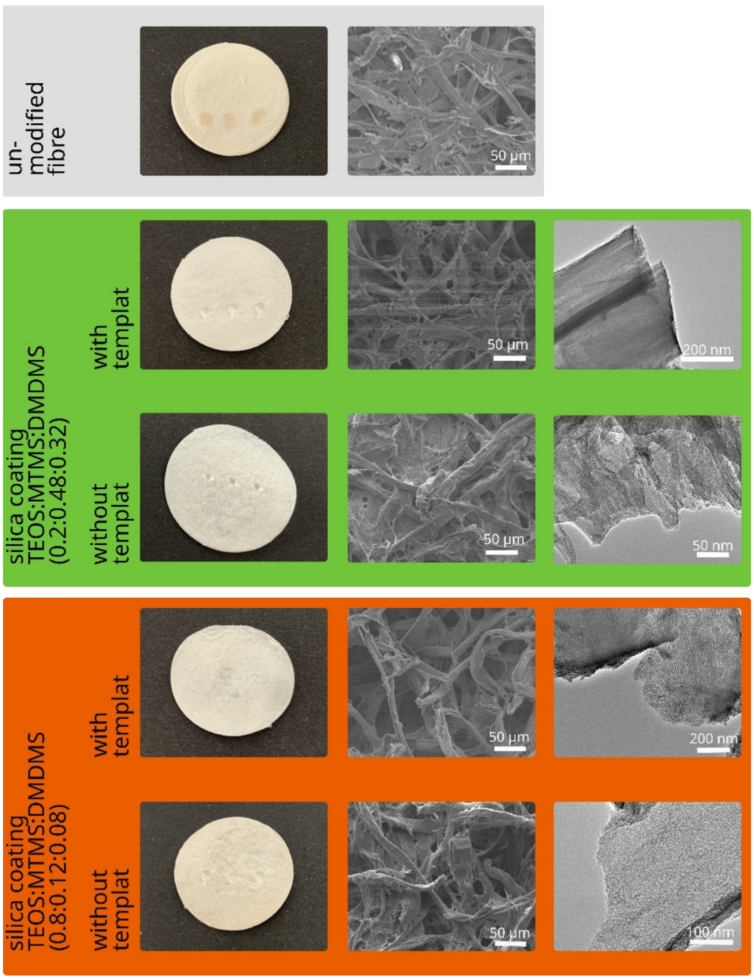


**Figure S 3:** SEM and TEM images of papers made of unmodified fibres and fibres with different silica coatings.

**Influence of the paper manufacturing process on the wettability of paper made of dense silica-functionalized fibres via fibre deposition**

For the paper manufacturing process, the fibres are deposited on a metal wire, and the freshly formed paper is dehydrated by applying a vacuum. Due to the sheet-forming process via fibre deposition at a metal wire, papers have a paper top (no contact with the metal wire) and a paper bottom side (in contact with the metal wire). To ensure the independence of the paper wettability from the manufacturing process, the static contact angle was measured at the paper top and at the paper bottom. Papers made of dense silica-coated cotton linter fibres manufactured by fibre deposition show comparable wettability at the top and bottom of the paper sides, and thus, the wettability is independent of the manufacturing process for dense silica-coated cotton linter fibres (**Figure S 4**).


**Figure S 4:** Wettability of small papers made of fibres with a dense silica coating. The 'close' and 'far' side of the sieve show a hydrophobic character which indicates that the paper production process does not influence the wettability of the paper.

**Paper grammage and silica coating amount of papers manufactured by fibre deposition**

Fibre pulp and paper specifications for the cotton linter fibres/papers before and after silica modification.

**Table S 2:** Fibre curl, external fibrillation degree, and fines content measured with a Valmet Fiber Image Analyzer FS5, (Valmet Oyi, Espoo, Finland) and the drain resistance of the refined cotton linter. Four measurements were performed with a Valmet Fiber Image Analyzer FS5, and the mean value and standard deviation are shown in the table.

| | Cotton linter refined [1.] Pulp |
|---|---|
| fibre curl | 14.9 ±0.2 % |
| external fibrillation degree [2.] | 1.8 ± 0.1 % |
| fines content [3.] | 17.5 ± 0.6 % |
| length-weighted average fibre length | 0.95 ± 0.01 mm |
| drainability [4.] | 23 ± 1°SR |

[1.] Laboratory refiner Voith LR 40; Specific edge load (SEL): 0.7 $Jm^{-1}$; Refining set: 3-1.6-60; Specific refining energy: 100 $kWht^{-1}$

[2.] The fibrillation rate is defined as the ratio of the area between the fibrils; these are connected to the fibre surface, and the total fibre area, including the main fibre and fibrils, scaled in percent (Laitinen et al. (2014)).

[3.] Percentage of the length-weighted distribution of the particles according to a length smaller than 0.2 mm.

[4.] Measured using the Shopper–Riegler method (ISO 5267-1:1999)

**Table S 3:** Grammage, apparent density, surface roughness and average porosity of unmodified cotton linter and paper made of cotton linter fibres with a dense silica coating.

| | cotton linter unmodified paper | cotton linter paper with dense silica coating |
|---|---|---|
| grammage | 67 ± 5 $gm^{-2}$ | 154 ± 24 $gm^{-2}$ |
| apparent density[6.] | 0.36 $gcm^{-3}$ | 0.19 $gcm^{-3}$ |
| surface roughness of the paper top side [5.] | 4.1 ± 01 µm | 13.7 ± 0.1 µm |
| average porosity[6.] | 76 ± 3 % | 87 ± 3 % |

[5.] The paper surface roughness was measured with a Keyence VR-5200 instrument using the arithmetic average of the 3D roughness after ISO 25178-2. An area of 43 $mm^2$ for three different samples was used for surface roughness determination, and shape correction was performed for elements larger than 2 mm.

[6.] The apparent density and average porosity were determined using the paper grammage (1.5 $gcm^{-3}$) and the paper thickness.

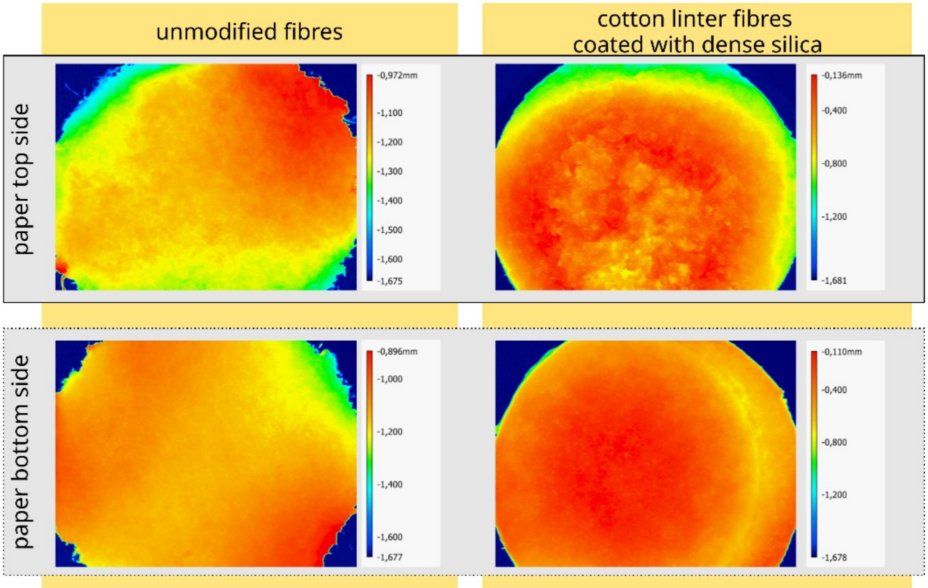


**Figure S 5:** Paper surface roughnesses of the paper top and bottom sides from paper made of unmodified fibres or fibres with a dense silica coating.

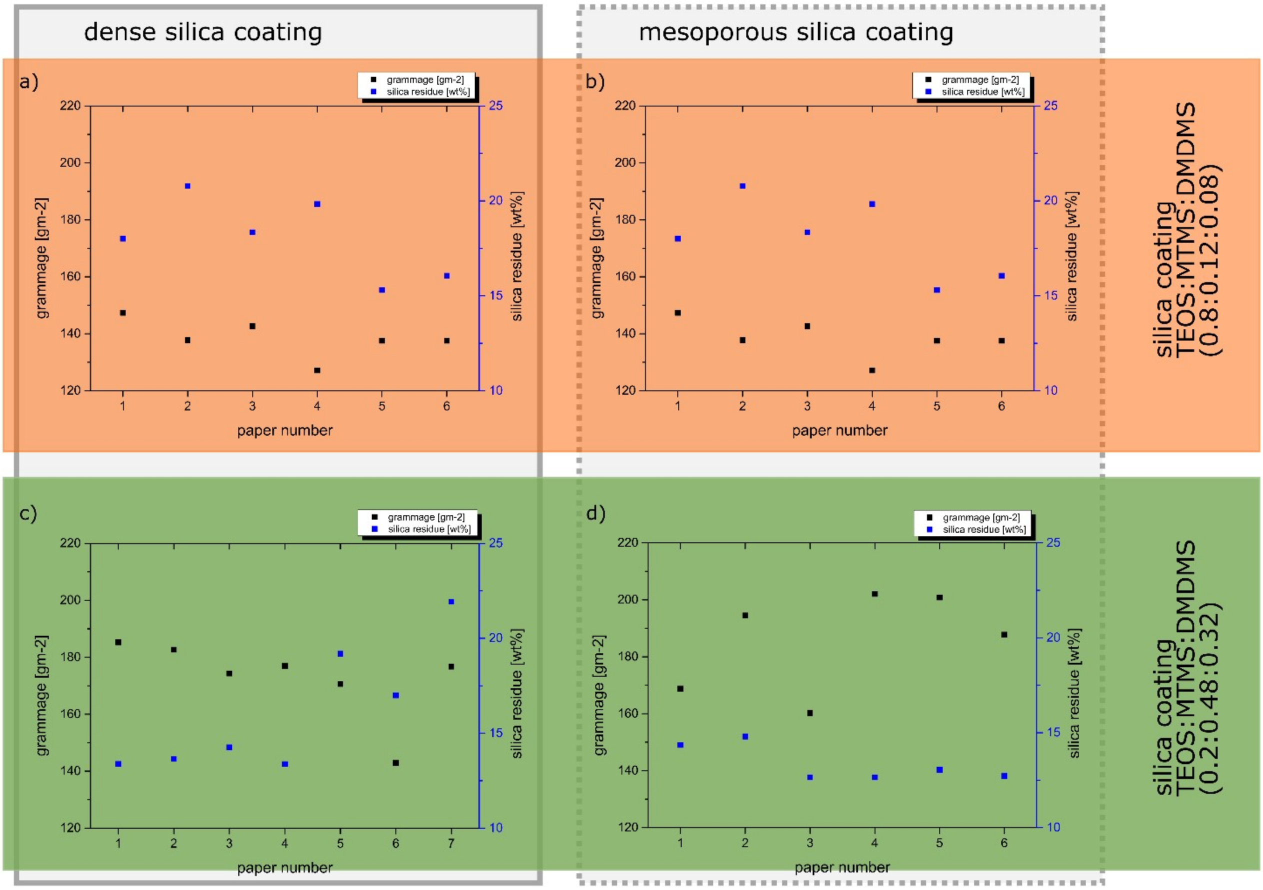


**Figure S 6:** Grammage and silica residue of the stir-coated fibres after sheet formation via fibre deposition.

**Mechanical properties of papers made of silica-coated fibres in dry and wet mode**

The mechanical stability was investigated by analysing the deformability of the papers prepared with different functionalized silica by supporting only half of the paper. In dry and wet mode, the papers do not deform or maintain their shape; thus, the silica coating does not affect the mechanical stability of the paper.

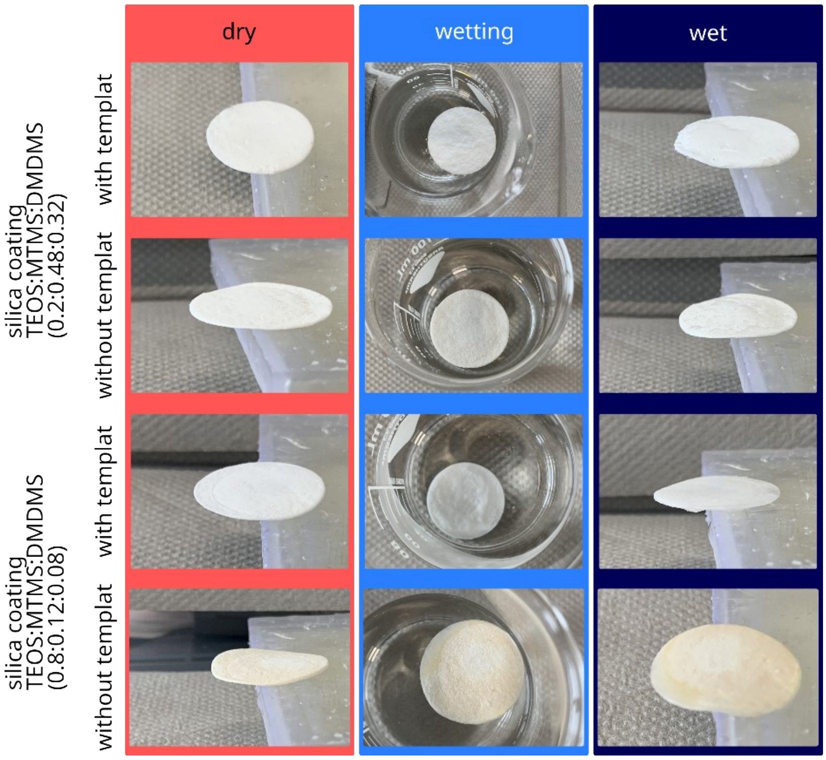


**Figure S 7:** Mechanical properties of the papers made of different silica-coated fibres in dry and wet mode as well as during the wetting process.

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