Influence of wetting on morphology and core content in electrospun core-sheath fibers Supporting Information

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Electrospinning set-up

A schematic drawing and a photo of the set-up are shown in Fig. S 1. A Fluigent MFCS microfluidic control unit was used to pump the sheath solution through a teflon tube to the metallic spinneret (inner diameter 0.7 mm, outer diameter 1.5 mm) and the core fluid was pumped by the same unit via a flexible silica capillary (inner diameter 0.35 mm, outer diameter 0.45 mm) inserted coaxially inside the spinneret. The core flow rate was varied from 0 to 1.2 mL/h while the sheath flow rate was kept fixed at 1.75 mL/h. A Gamma High Voltage power supply was used to deliver the (positive) voltage to the metallic outer capillary via a crocodile clip, as seen in the photo in Fig. S 1. The distance from spinneret

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to a grounded counter electrode was 15 cm and the applied voltage was 10 kV. Inside the spinning chamber the temperature was 24°C and the relative humidity 20%.

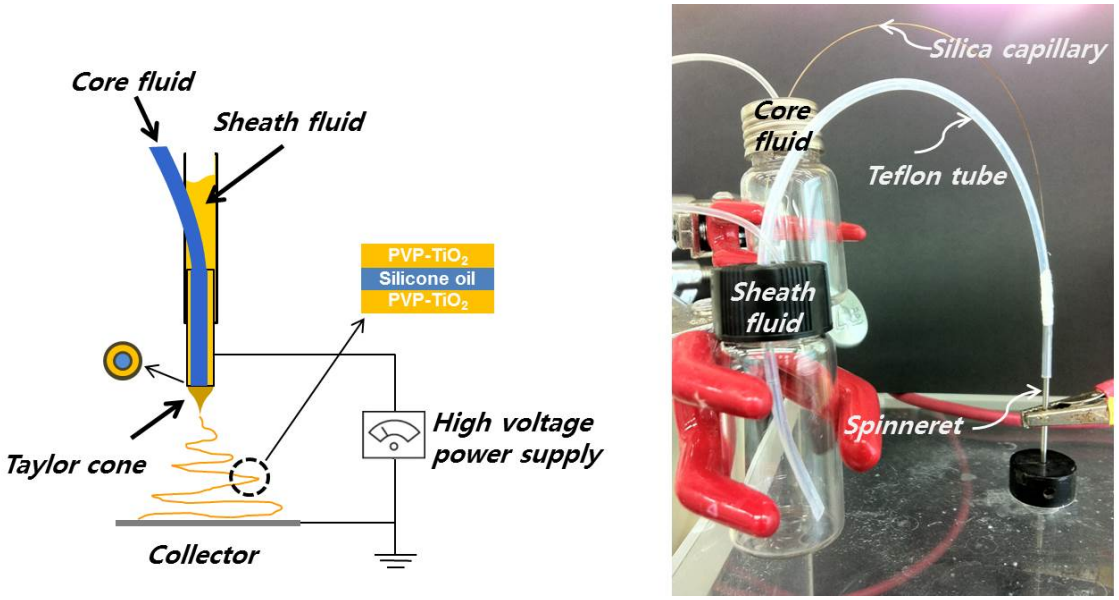

Figure 1: Schematic drawing of the coaxial electrospinning experiment (left) and photo of the spinneret (right) .

Electron microscopy imaging of the fiber cross section and chemical characterization by energy dispersive X-ray spectroscopy

The first view of the fiber cross sections was achieved by cutting through the fibers using FIB, following the procedure of Enz et al.,[1] and then image the exposed cross section with Scanning Electron Microscopy (SEM). Prior to cutting the fibers were coated with a layer of platinum. The resulting images, for the four fibers investigated on hydrophobic substrates and two fibers investigated on hydrophilic substrates, are shown in Fig. S 2. Many of the features discussed in the main article are detectable in these images, albeit with less detail and without information on chemical constitution.

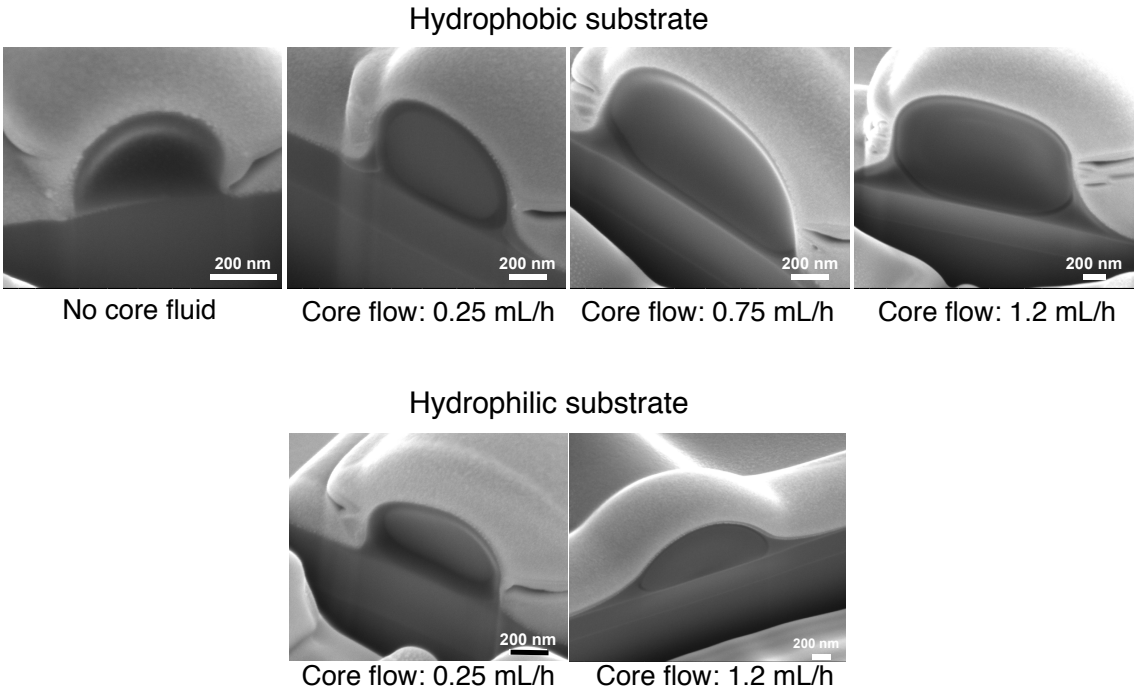

Figure 2: SEM images of fiber cross sections revealed by cutting through fibers using FIB.

More details were resolved by HR-TEM imaging of slices produced by FIB lift-out. One example for each fiber type is shown in the main paper, in that case with all surrounding materials removed digitally. The original images of all slices investigated are shown, together with relevant size measures, in Fig. S 3. The locations in the fibers where the slices were taken are shown in the main paper for deposition on hydrophobic substrates, and for hydrophilic substrates they are shown in Fig. S 4.

The cross section images of the largest fibers deposited on hydrophobic substrate reveal that the bottom of the sheath is expanded around the center, compared to the top and sides. In fact, the PVP has cracked in this regime in both cross sections studied, with voids appearing between polymer and substrate, and in some cases an expansion into a sponge-like structure can be seen. The origin of these local variations in sheath morphology is most likely the difficulty for the chloroform contained in the central bottom sheath region upon fiber deposition to escape. Direct evaporation is impossible due to the substrate and at the sides the water meniscus blocks chloroform evaporation, requiring the solvent to leave this part of

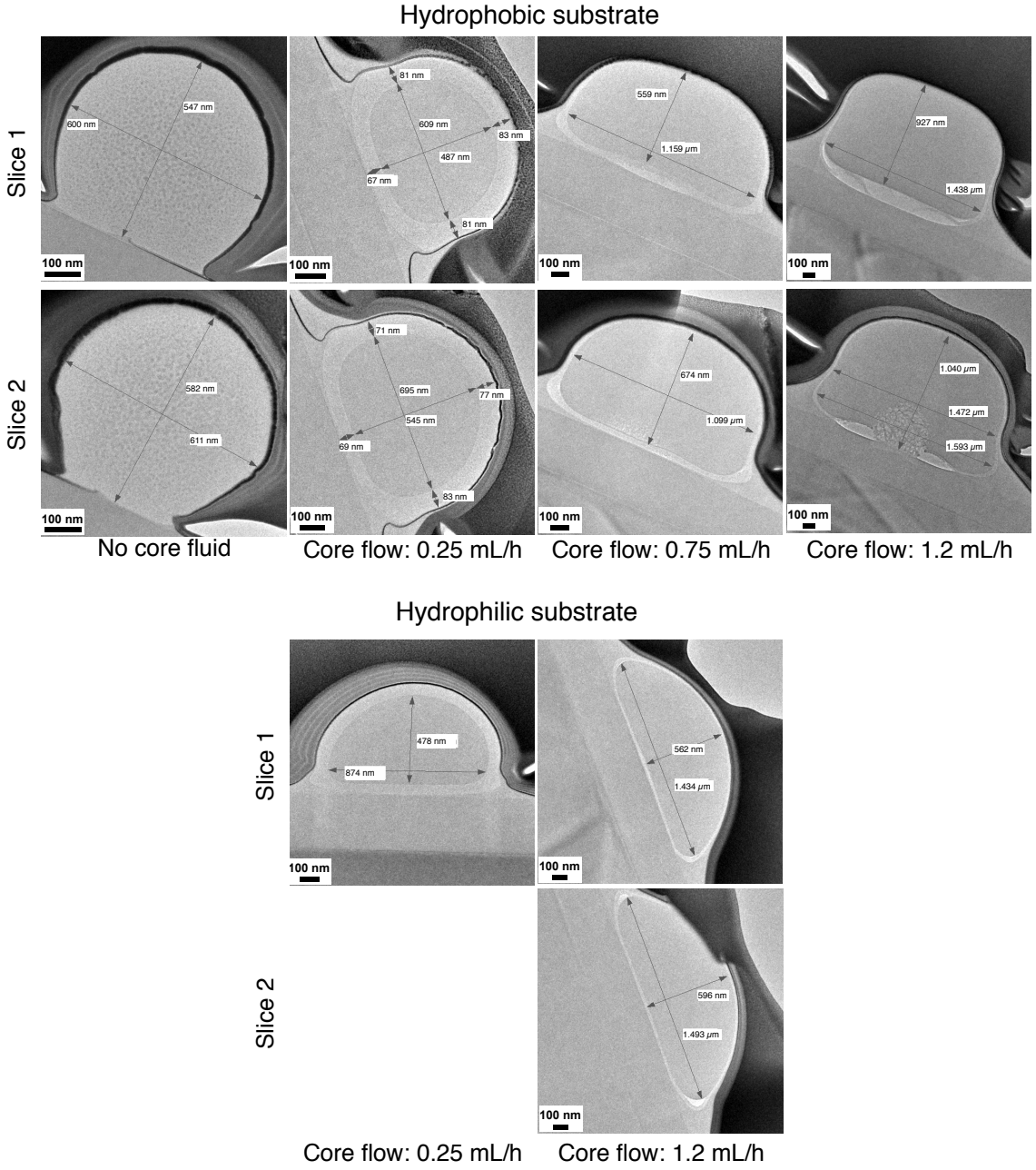

Figure 3: HR-TEM images of all slices lifted out from fibers using FIB, together with the horizontal and vertical extensions of core and, for the 0.25 mL/h core flow fibers, sheath.

the sheath slowly by diffusion through the silicone oil above it. The considerable time thus required for solvent removal from the sheath bottom leads to very slow de-swelling of the PVP there. Capillary forces maintain the liquid silicone oil as a single volume everywhere in contact with the sheath, which will solidify faster on the top and along the sides than at the bottom, which will remain soft substantially longer. As the core liquid volume continuously decreases through solvent evaporation its lower boundary thus rises, pulling the bottom sheath with it. At the same time, it adheres to the solid substrate below, resulting in a frustrated situation which breaks up the slowly solidifying bottom PVP sheath into a foam-like structure with voids of varying size. The same phenomenon has been observed in single-fluid electrospinning, albeit much less localized.[2]

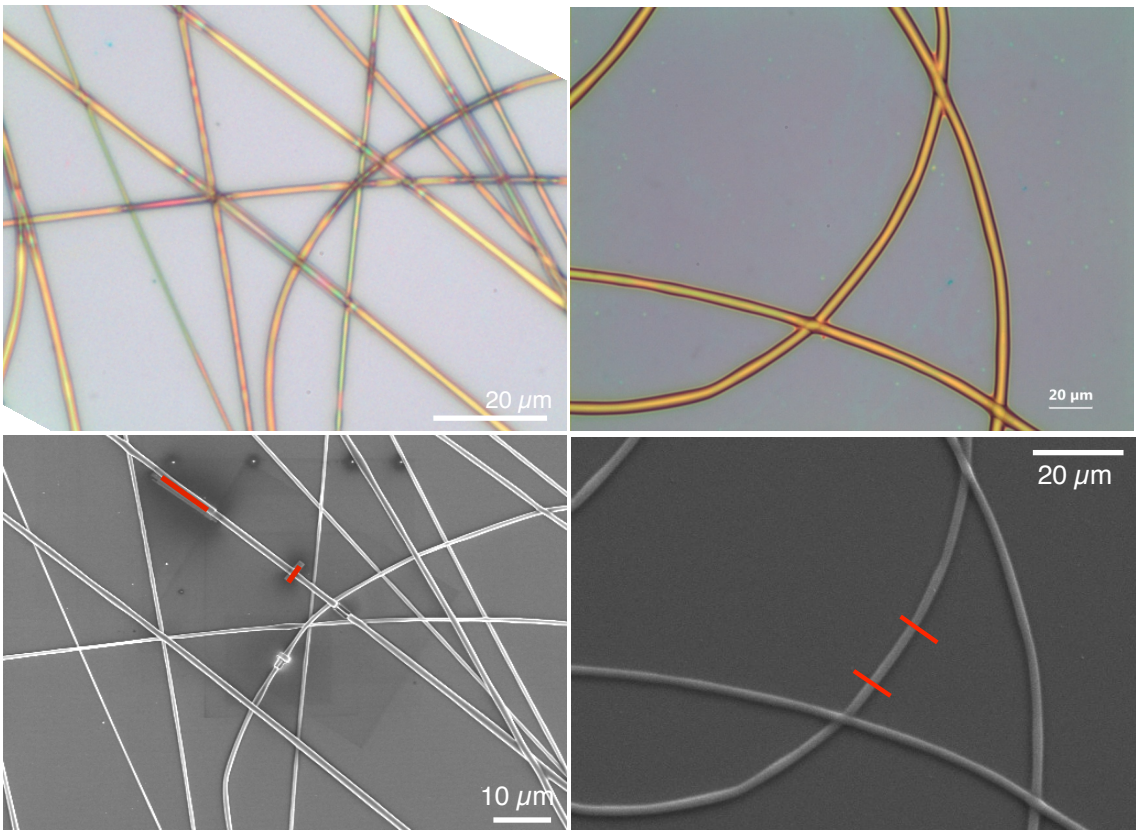

Figure 4: Overview images of fibers deposited on a hydrophilic silicon chip, as seen by reflection optical microscopy (top) and SEM (bottom). The locations where slices were lifted out by FIB for HR-TEM imaging are indicated by red lines in the SEM images.

In order to get a picture of the continuity of the core along the fiber, a slice was lifted out using FIB also along one fiber and this was analyzed by HR-TEM and EDS, see Fig. S 5. The core is clearly very continuous, with negligible variations of the bottom sheath thickness. Unfortunately the fiber top could not be resolved cleanly in this cut since the fiber sheath collapsed somewhat along the top, despite the stabilizing platinum coating.

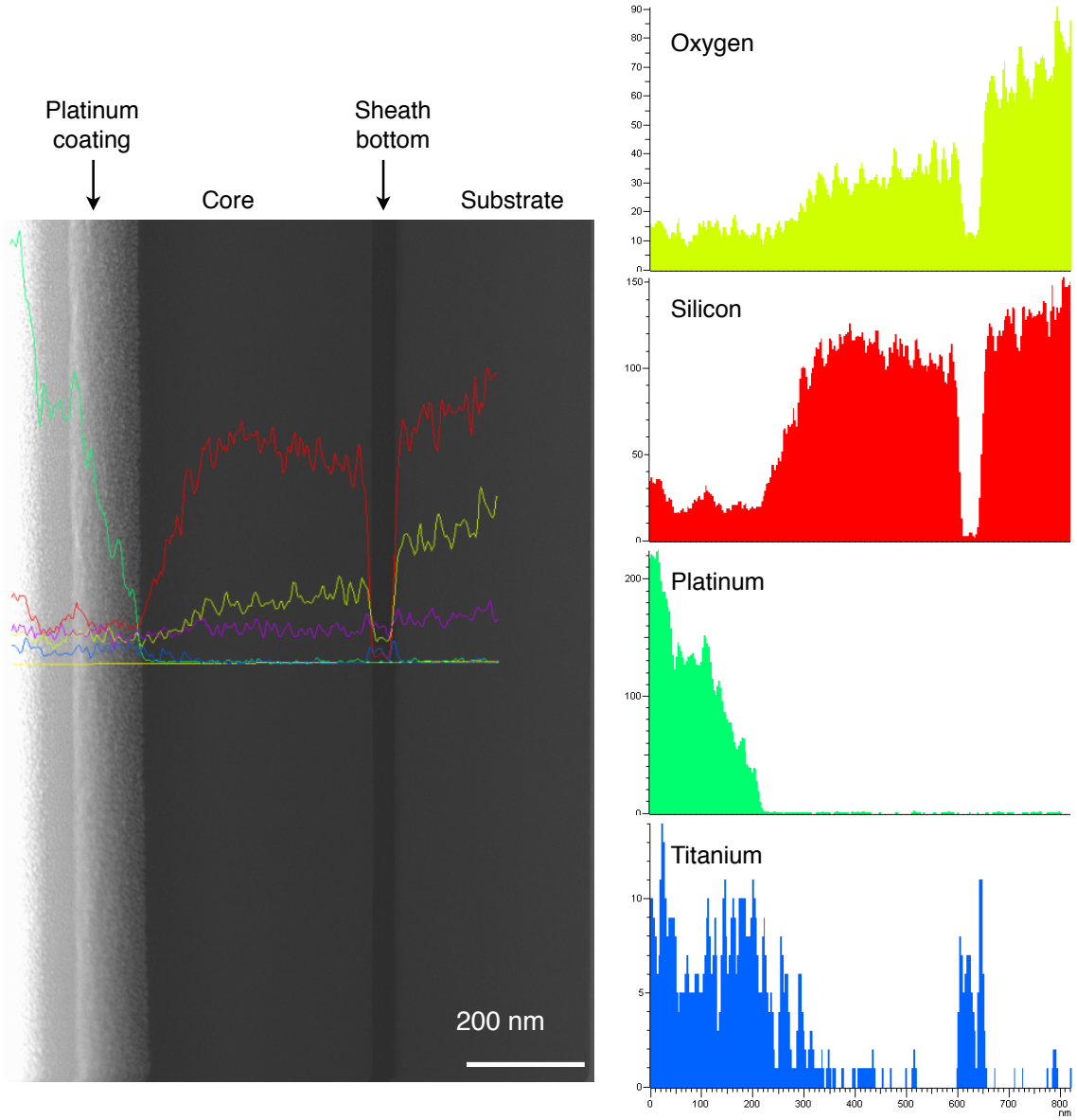

Figure 5: HR-TEM image (left) and EDS chemical analysis (individual spectra on the right and superimposed on TEM image on the left) of a longitudinal slice of a fiber spun with 0.25 mL/h core flow rate and deposited on a hydrophilic silicon substrate.

The EDS scan through the fiber spun without core fluid is shown in Fig. S 6. The concentration of TiO_2 particles and increase in particle size towards the center of the fiber cross section is easily seen.

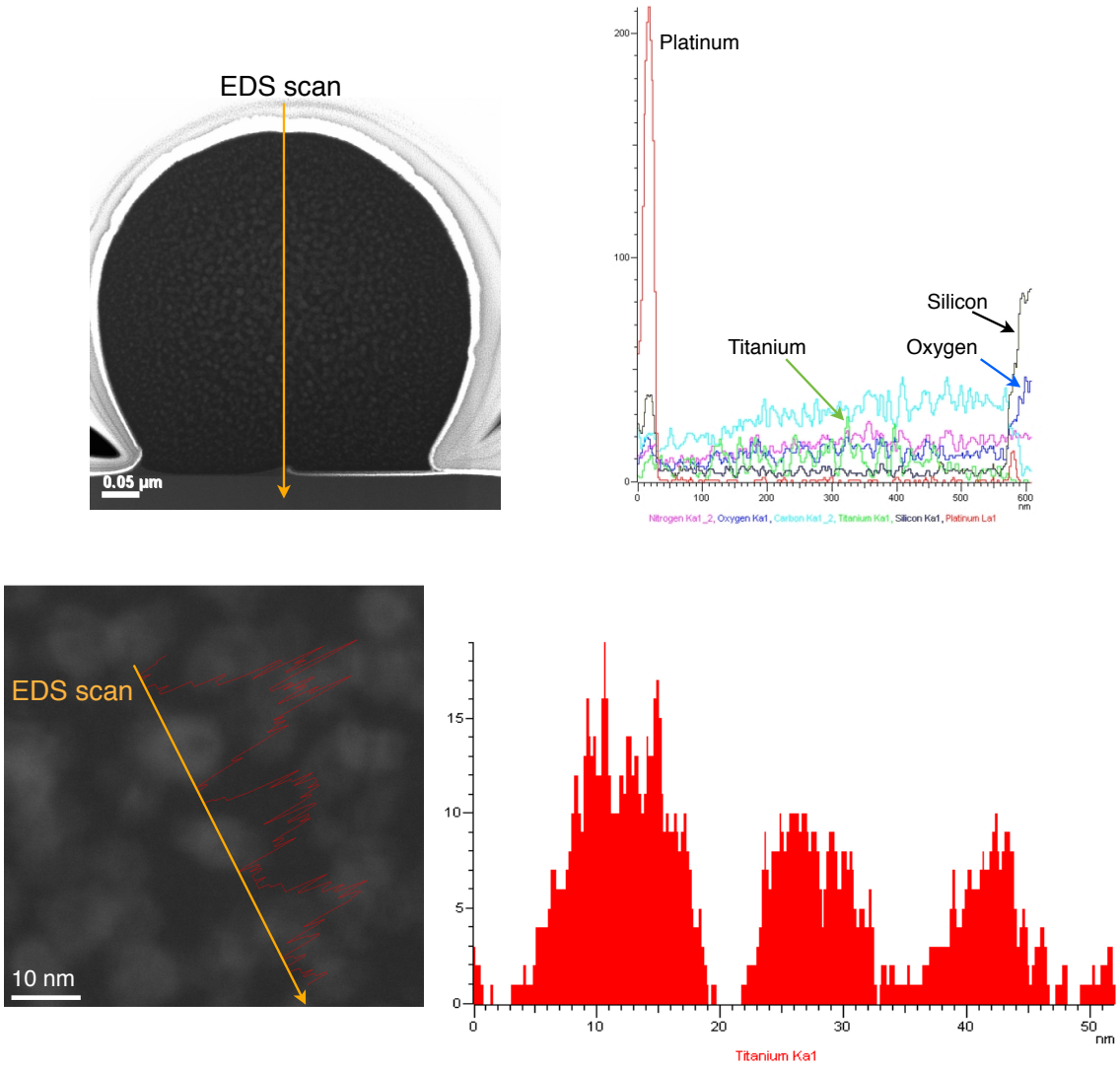

Figure 6: HR-TEM images and EDS chemical analysis of a cross section slice produced by FIB lift-out through the fiber spun without core fluid. At the top the results of a vertical EDS scan through the whole fiber cross section is shown, at the bottom a zoomed-in scan close to the cross section center.

FIB lift-out procedure

After positioning the sample previously characterized by SEM in the high vacuum chamber of the FIB (Quanta 3D FEG) the region of the fiber selected for slicing was coated with a second supporting platinum layer, whereafter the surrounding material on both sides of the slice was removed using FIB milling (Gd^+ ions, 30 kV, 3-50 nA). Once a thin enough slice had been achieved (about 70 nm) this was cut out from the substrate and transferred inside the FIB chamber to a TEM grid. After a final FIB polishing the specimen appearance was as in Fig. S 7. It was then removed from the FIB chamber and inserted in the HR-TEM (JEOL JEM-2100F) high vacuum chamber for imaging.

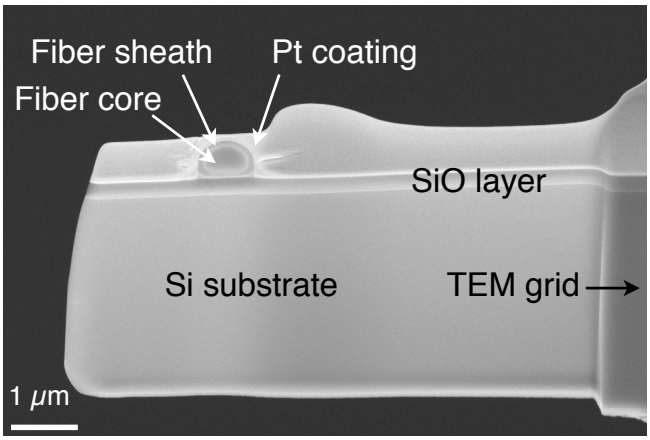

Figure 7: SEM image of a sample prepared for HR-TEM investigation by FIB milling lift-out.

It may seem surprising that liquid silicone oil remains at the core of the fiber slice even in the high-vacuum environment of the HR-TEM and that the thin liquid film that it effectively constitutes in the FIB-prepared slice does not break. However, silicone oil is a quite unusual liquid with two peculiar properties that render it very suitable for this type of investigation. First, the high molecular mass of the oil used in our experiments leads to a vapour pressure that is fully negligible, preventing evaporation of this polymeric liquid even under high-vacuum condition. Second, its rather high viscosity, combined with the negligible evaporation, allows silicone oil to form a stable free-hanging film if suspended by an appropriate closed frame. In this case the slice of the sheath and the surrounding

stabilising platinum coating and silicon substrate form the frame that prevents the film from breaking up into a droplet.

Contact angle measurements

All liquids used in the experiment were tested for their wetting ability of the two types of silicon substrate used in the experiments, see Fig. S 8. Silicone oil as well as the sheath solution both wet both substrates, while water exhibits mainly wetting characteristics on the hydrophilic substrate (contact angle 47°) but clearly non-wetting behavior on the hydrophobic one (contact angle 104°).

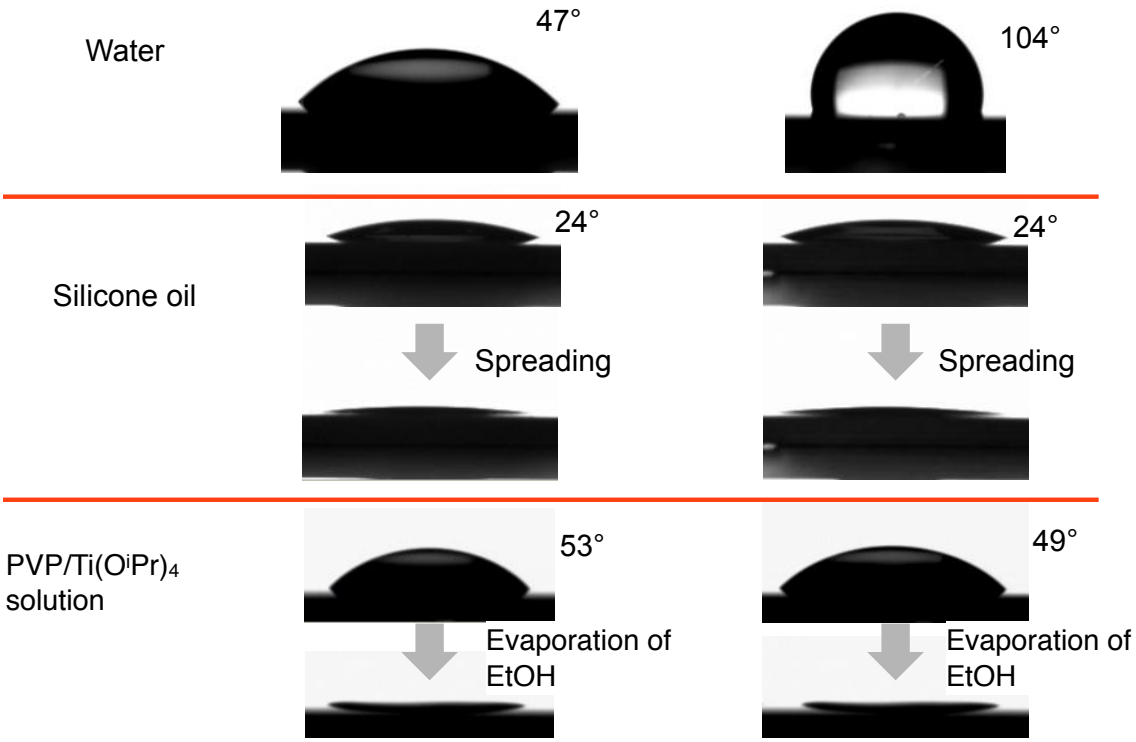

Figure 8: Contact angle measurements of all liquids involved in the experiments, on the hydrophilic (left column) and hydrophobic (right column) silicon substrates.

Hydrophobic surface treatment

Surfaces were treated for hydrophobic behavior following the procedure of reference.[3] In brief, the substrates were cleaned (5 min. sonication in isopropyl alcohol) and treated with UV oxygen plasma (25 W, 20 minutes), followed by immersion in a 0.1 wt% aqueous solution of 3-aminopropyltriethoxysilane (Aldrich) for 10 min. to create an aminosilanized surface. Monoglycidyl ether terminated polydimethylsiloxane ($M_n = 5,000$ g/mol, Aldrich) was dripped on the substrates which were then baked at 80°C for 4 hours. Unreacted siloxane was removed with isopropyl alcohol.

Viscosity measurements

The shear viscosity as a function of shear rate is shown for the sheath solution, pure silicone oil, and two mixtures of silicone oil and chloroform in Fig. S 9.

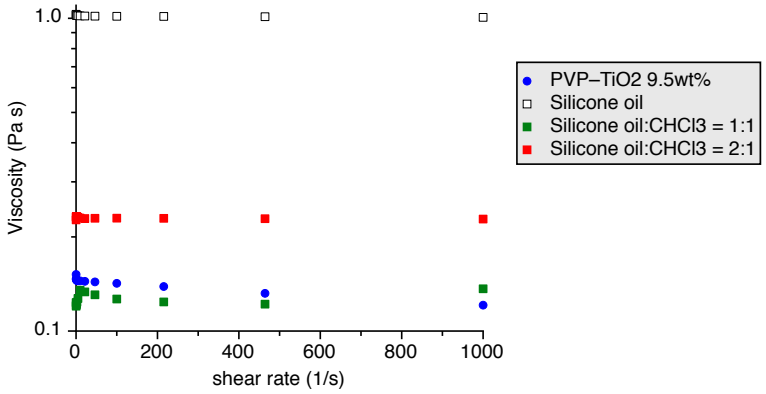

Figure 9: Shear viscosities of sheath solution and three potential core fluids.

References

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2. Arinstein, A.; Zussman, E. Electrospun Polymer Nanofibers: Mechanical and Thermodynamic Perspectives. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 691–707.

3. Kim, S.; Cui, Y.; Lee, M.; Nam, S.; Oh, D.; Kang, S.; Kim, Y.; Park, S. Simple Fabrication of Hydrophilic Nanochannels Using the Chemical Bonding Between Activated Ultrathin PDMS Layer and Cover Glass by Oxygen Plasma. *Lab Chip* **2011**, *11*, 348–353.