ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Paper-Based Surfaces with Extreme Wettabilities for Novel, Open-Channel Microfluidic Devices

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Note 1. Capillary flow on multiplexed fluoro-paper A

Seven different liquids were selected to demonstrate the capability of the O_2 plasma patterning technique, covering both polar and non-polar liquids, with surface tensions γ_{lv} = 18.4–72.8 mN/m (at 20 °C) (Table S1). Seven straight channels 50 mm long × 2 mm wide were fabricated on each fluoro-paper A substrate (390 μm thick) (Methods; Figure S4). 20 μL droplets of each of the seven test liquids were then placed at the end of its corresponding channel, and the lateral flow behavior under room temperature and atmospheric pressure was observed (Figure S5a). Three parameters, which directly relate to device design and applications, were systematically studied: maximum wetting length in the channel (Table S3), average wetting velocity (maximum wetting length divided by the total wetting time) (Table S4), and wetting depth (the vertical distance the liquid wets into the channel) (Table S5, Figure S5b).

The wetting length of a liquid in a capillary tube is described by Washburn's equation as follows[31]

$$L^2 = \frac{\gamma D t \cos\theta}{4\eta}$$

here L is the wetting length, γ is the liquid surface tension, D is the capillary diameter, θ is the contact angle, and η is the viscosity of the liquid. If the capillary tube is fully wettable, $\theta = 0°$, and the average wetting velocity of capillary flow ($\Delta L/\Delta t$) for the seven test liquids should increase with increasing surface-tension to viscosity ratio (γ/η) as follows (Table S1): acetone > water > hexane > chloroform > DMF > ethanol > hexadecane.

However, etching fluoro-paper A for 5–900 sec did not produce a surface with simultaneously high wetting rates for all liquids, nor one that exhibited variation in wetting rates consistent with Washburn's equation. For all etching times, the channels exhibited some finite resistance to wetting by at least one of the liquids. This is further evidence for the fluorine redeposition effect that selectively reduces the wettability and wetting rates for nonpolar liquids after extended O_2 plasma etching times, rather than continually increasing the solid surface energy and thereby increasing the wetting rates for all liquids.

Moreover, it should be noted that, for each of the seven test liquids, the average wetting velocity (total wetting length L divided by total time t) reached a peak value within the O_2 plasma etching times tested (Table S3). The decline in wetting rate after the peak value can be attributed to the fluorine recovery effect on wettability as discussed in the main manuscript.

A similar peak was also observed for maximum wetting length versus etching time for each liquid (Table S2). For certain liquids, especially those with relatively low boiling points, the maximum wetting length was found to be strongly influenced by evaporation. Acetone, chloroform, and hexane could not fill an entire 50 mm long channel with 20 μL of test liquid, even when their optimal wetting velocity was achieved. In comparison, liquids such as water, DMF, and ethanol with relatively high boiling points could fill 50 mm channels over a wide range of etching times (Table S1; Figure S5a).

Note 2. Optimization of three-dimensional channels on fluoro-paper A

First, a set of three-dimensional channels with one bridge each was prepared (Figure S6a). When added to one end of each of the channels, water, DMF, ethanol, and heptane all smoothly transferred through the bridge, reaching the other side (Figure S6b-d). The O_2 plasma etching (200 W) times for each single-bridge channel were 900 sec for water, 120 sec for DMF and ethanol, and 15 sec for heptane, longer than those required for simple two-dimensional channels. O_2 plasma power had to be increased to 350 W to produce three-dimensional channels with

multiple bridges. A set of channels with two bridges each were prepared, and wetting time was characterized with the four test liquids previously mentioned. The etching times at 350 W were optimized so that the liquids would completely wet the channels in the minimum possible time: 300 sec for water, 60 sec for DMF, 15 sec for ethanol, and 30 sec for heptane.

Based on the optimized 350 W O_2 plasma treatment for channels with two bridges each, finally a set of channels with four bridges each was prepared with perpendicular channels underneath the bridges (shown in main text, Figure 2a-c). The optimized etching times for this geometry were: 180 sec for water channels, 60 sec for DMF channels, 30 sec for heptane channels, and 15 sec for ethanol channels.

Table S1. Liquid properties (surface tension, viscosity, polarity index, boiling point) of the seven test liquids.

	Water	**DMF**	**Chloroform**	**Acetone**	**Ethanol**	**Hexane**	**Hexadecane**
Surface tension [mN/m at 20 °C]	72.8	36.8	27.2	23.3	22.3	18.4	27.5
Viscosity [mPa·s at 20 °C]	1.00	0.92	0.57	0.31	1.10	0.31	3.01 (25 °C)
Polarity index	10.2	6.4	4.1	5.1	5.2	0.1	0.1
Boiling point [°C]	100.0	152.0	61.2	56.0	78.4	68.7	271.0

Table S2. θ^*_{adv}, θ^*_{rec} and contact angle hysteresis ($\Delta\theta$) values for various liquids on fluoro-paper A.

Solvent	γ_{lv} [mN/m at 20 °C]	θ^*_{adv} [°]	θ^*_{rec} [°]	$\Delta\theta$ [°]
Water	72.7	161	143	19
Propylene Glycol	45.6	150	122	28
N,N-Dimethylformamide	34.4	143	100	43
o-Xylene	29.6	138	97	40
Hexadecane	27.1	136	103	33
Chloroform	26.7	126	90	36
Tetrahydrofuran	26.7	125	90	36
Acetone	23	121	84	37
Methanol	22.1	114	60	54
Ethanol	22	112	59	53
1-Propanol	20.9	113	60	52
Hexane	17.9	91	35	57

Table S3. Maximum wetting length, *i.e.* the maximum horizontal distance that the liquid front covers, for 20 μL of test liquid placed into channels on fluoro-paper A. The liquid channels are 50 mm in length.

O_2 plasma etching time at 200 W [sec]	Maximum wetting length [mm]						
	Water	**DMF**	**Chloroform**	**Acetone**	**Ethanol**	**Hexane**	**Hexadecane**
5	4.0	7.2	9.6	11.6	16.0	25.0	6.9
15	5.8	36.4	23.5	42.7	50	39.5	33.5
30	10.7	50	21.5	43.7	50	40.5	23.6
60	50	50	20.0	45.5	50	42.6	24.6
120	50	50	34.5	42.5	50	38.6	21.4
300	50	50	13.0	30.9	37.6	25.5	3.8
600	50	50	13.6	27.0	35.2	22.1	3.8
900	50	50	14.2	21.4	31.8	3.8	3.8

Table S4. Average wetting velocity, *i.e.* maximum wetting length divided by the total wetting time.

O_2 plasma etching time at 200 W [sec]	Average wetting velocity [mm/s]						
	Water	**DMF**	**Chloroform**	**Acetone**	**Ethanol**	**Hexane**	**Hexadecane**
5	0	0	0	0.50	0.43	1.04	0
15	0	0.14	0.56	2.03	2.27	1.88	0.08
30	0.47	1.35	0.50	2.43	2.63	2.25	0.06
60	0.16	1.67	0.21	2.28	1.85	2.84	0.05
120	0.81	1.00	0.82	2.66	1.39	2.27	0.01
300	0.25	0.61	0.14	1.82	0.63	1.70	0
600	0.15	0.16	0.10	0.73	0.35	0.88	0
900	0.15	0.10	0.12	0.40	0.25	0	0

Table S5. Wetting depth, *i.e.* the vertical distance that the test liquid wets within the channel. The thickness of paper is 390 μm.

O_2 plasma etching time at 200 W [sec]	Wetting depth [μm]						
	Water	**DMF**	**Chloroform**	**Acetone**	**Ethanol**	**Hexane**	**Hexadecane**
5	52	75	94	66	56	94	28
15	65	94	103	81	85	108	66
30	93	101	92	69	70	149	58
60	85	160	89	240	273	211	94
120	116	202	99	273	287	226	99
300	160	273	197	282	301	230	216
600	183	291	240	318	321	291	150
900	211	305	245	339	341	310	211

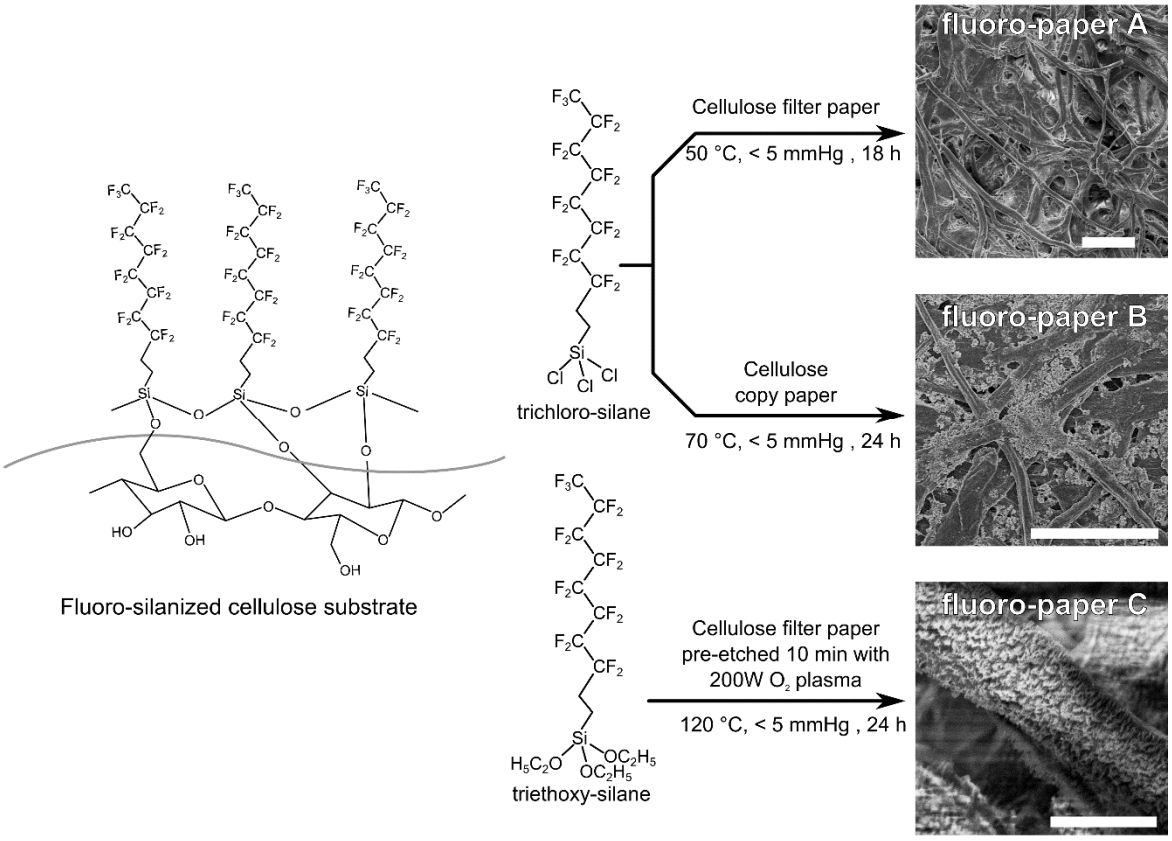

Figure S1. Fluoro-silanization of different cellulose papers by vapor phase deposition. Typical SEM images of cellulose filter paper (A), cellulose copy paper (B) and cellulose filter paper pretreated by O_2 plasma etching (Plasmatherm 790, 200 W, 10 min) (C). Scale bars on SEMs of Type A, B, and C are 100, 100, and 10 μm respectively.

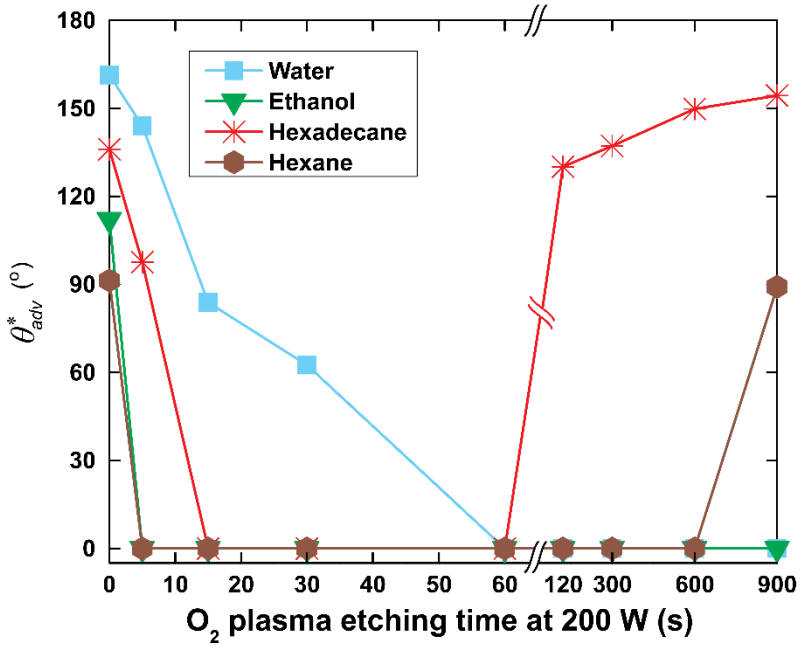

Figure S2. θ^*_{adv} values for various liquids on fluoro-paper A treated by O_2 plasma etching for varying times (0–900 sec).

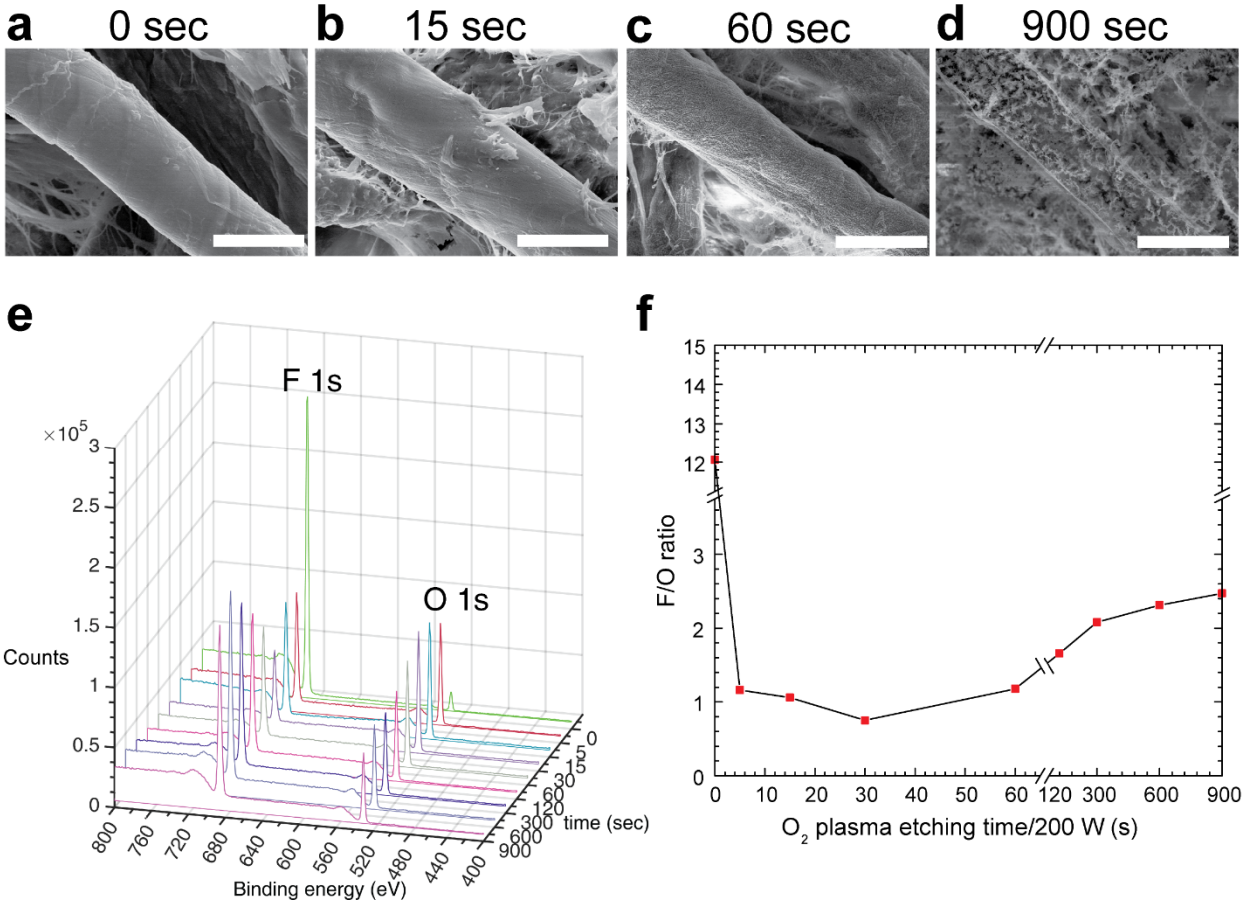

Figure S3. (a-d) SEM images and XPS peak data for fluoro-paper A treated by O_2 plasma etching for different times (0–900 sec) showing the dramatic change in the fiber surface texture. All scalebars are 10 µm. **(e)** XPS spectra at various etching times, with the fluorine 1s and oxygen 1s peaks highlighted. Note the rapid initial decrease in fluorine content and increase in oxygen content as the fluorosilane is replaced by oxygen-rich species from the reactive oxygen plasma. At extended etching times, the redeposition of fluorocarbon fragments on the O_2 plasma-etched surface is visible as an increase in the fluorine 1s peak and a decrease in the oxygen 1s peak. The ratio between the peak heights for fluorine and oxygen versus time are plotted in **(f)**.

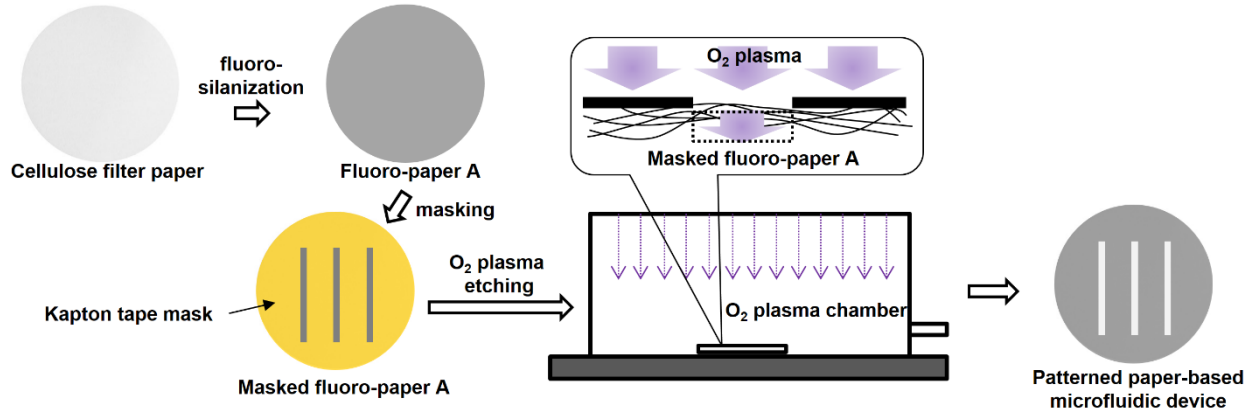

Figure S4. Schematic illustration of the procedure to make a wettability-patterned paper device by selective O_2 plasma etching of fluoro-paper A.

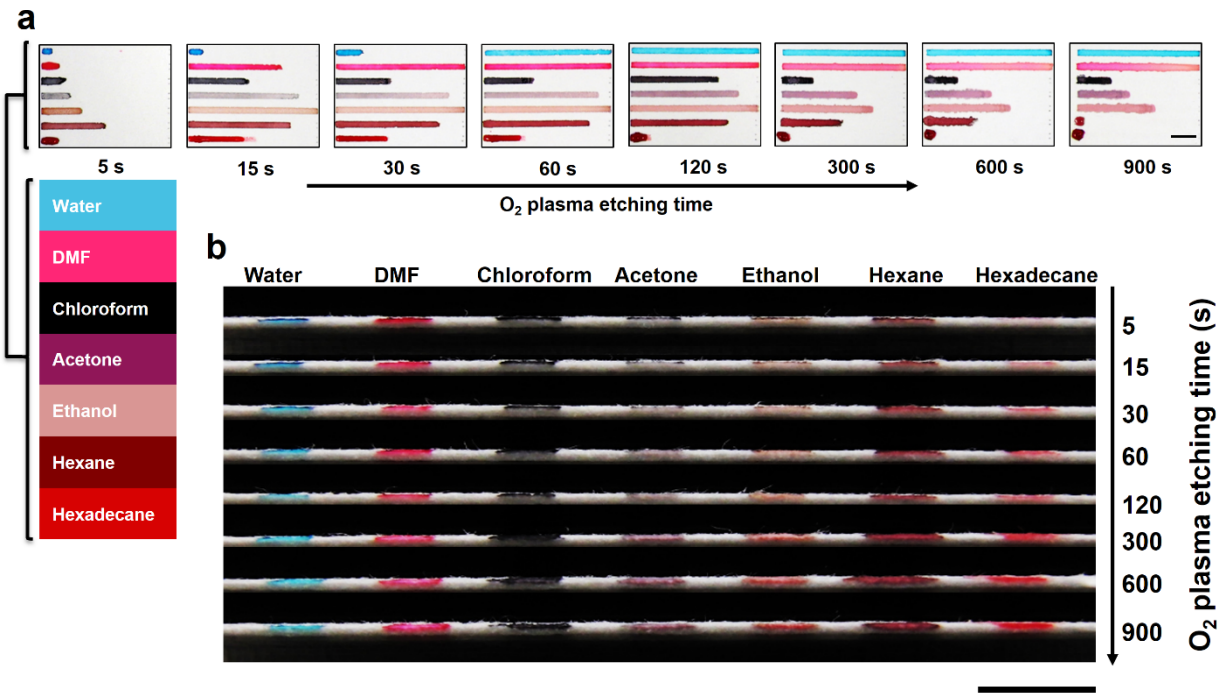

Figure S5. Lateral flow in two-dimensional channels treated by 200 W O_2 plasma etching for varying times on fluoro-paper A. **(a)** Fluoro-paper A devices with straight 50 mm × 2 mm channels that were treated by O_2 plasma with etching times between 5 and 900 sec. For different paper devices exposed for each time (increasing from top to bottom), water (blue), DMF (pink), chloroform (black), acetone (light purple), ethanol (light pink), hexane (maroon), and hexadecane (dark red) were tested. The paper substrates were positioned horizontally and each channel was filled with 20 µL of test liquid. Scale bar is 1 cm. **(b)** Optical image of the cross-section of two-dimensional channels etched for various times filled with seven test liquids. The paper thickness is 390 µm, scale bar is 5 mm.

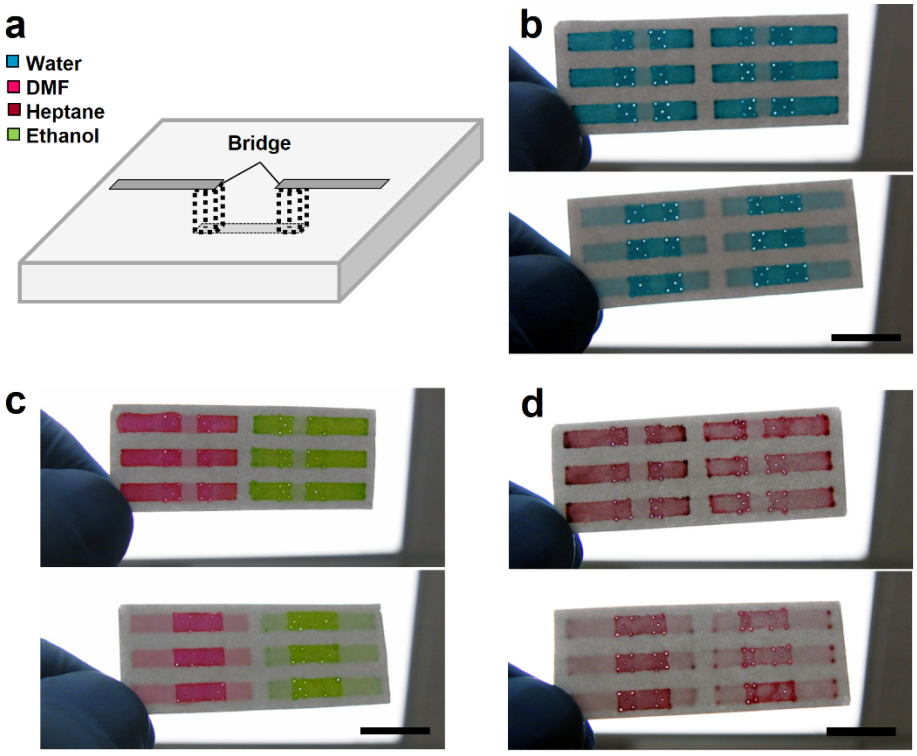

Figure S6. (a) Schematic illustration of three-dimensional channels each with a single bridge (fluoro-paper A). The channels are 18 mm long × 2 mm wide. Each bridge was 7.5 mm long and contained an array of five 500 μm diameter perforations on either side. **(b)** Three-dimensional channels filled with water (dyed blue). **(c)** Three-dimensional channels filled with DMF (dyed pink) and ethanol (dyed green). **(d)** Three-dimensional channels filled with heptane (dyed maroon). Scale bars are 1 cm.

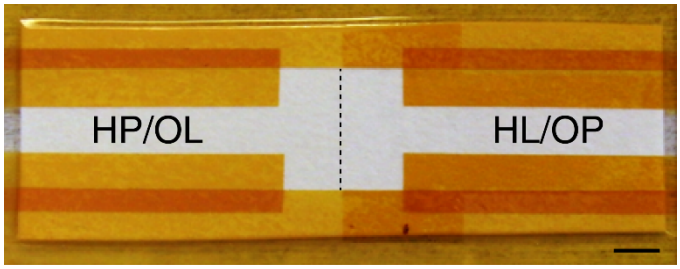

Figure S7. Geometry of the device for continuous surface oil-water separation (fluoro-paper A). The HP/OL channel was O_2 plasma etched at 200 W for 15 sec, while the HL/OP channel was etched for 900 sec. Scale bar is 5 mm.

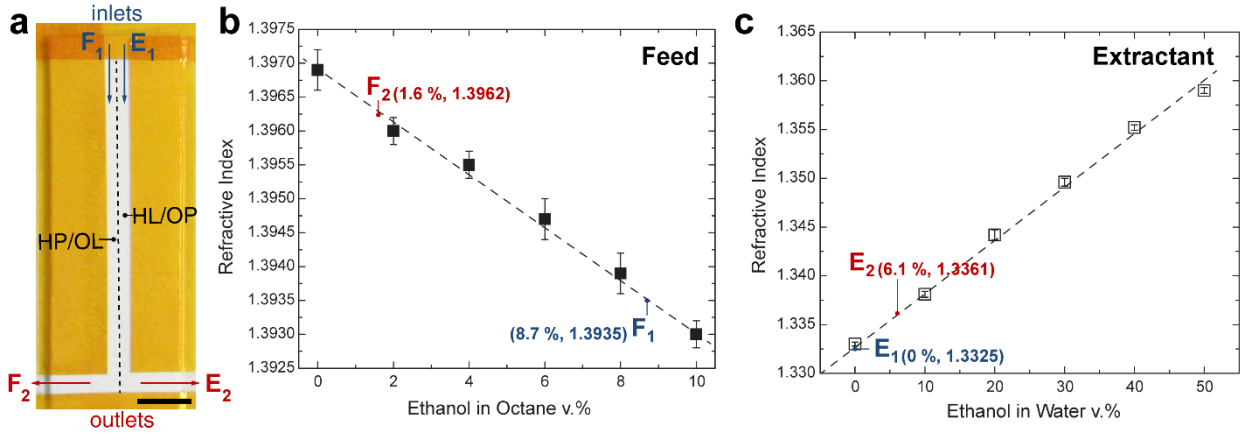

Figure S8. (a) Geometry of the device for continuous surface liquid-liquid extraction (fluoro-paper A). The HP/OL channel was etched at 200 W for 15 sec, and the HL/OP channel was etched for 900 sec. Scale bar is 1 cm. **(b, c)** Refractive index measurements of the feed and extractant before (F_1, E_1) and after extraction (F_2, E_2). A calibration curve for each mixture was first obtained by measuring mixtures of known composition (black data points), which was then used to quantify the composition of the test samples.

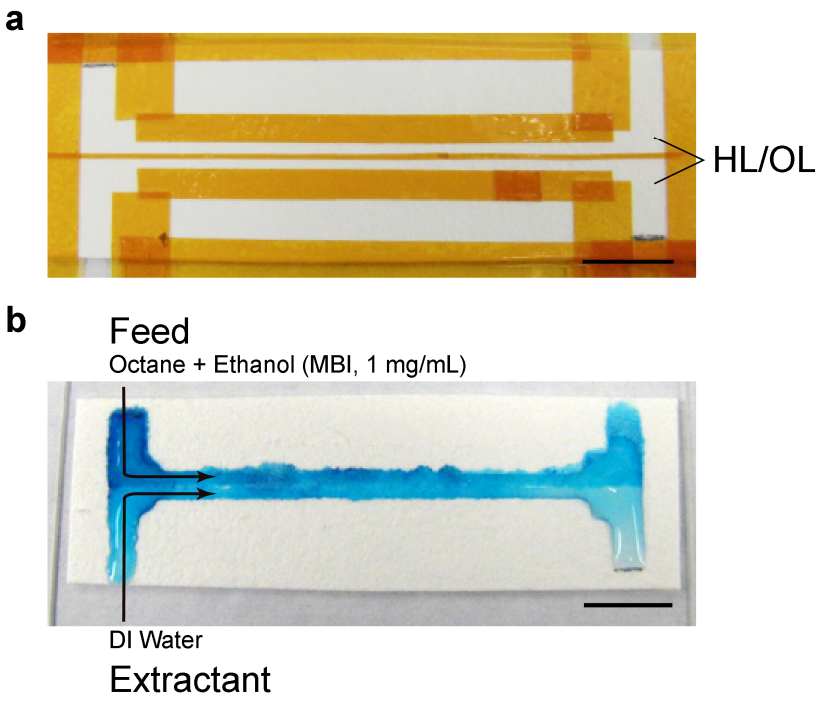

Figure S9. Control experiment for liquid-liquid extraction. **(a)** Geometry of side-by-side omniphilic channels patterned on fluoro-paper A, with 200 W O_2 plasma etching for 120 sec. **(b)** Failure to form a clear and stable oil-water interface between the feed and the extractant in the absence of channels possessing selective wettability. Scale bars are 1 cm.

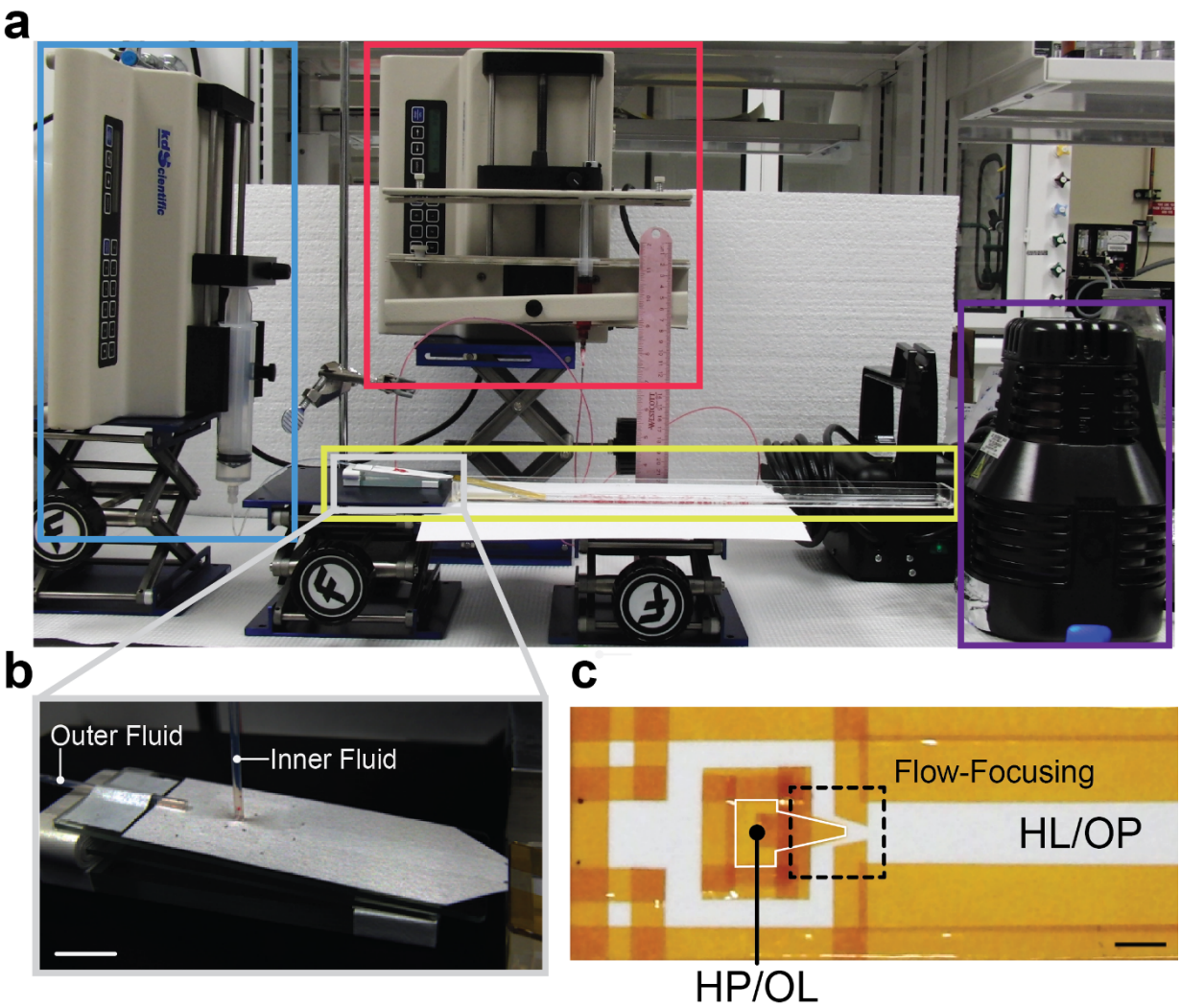

Figure S10. (a) Surface emulsification apparatus. The syringe pump highlighted in blue is used to control the flow rate of the outer carrier fluid. The other pump, highlighted in red, controls the inner precursor fluid. The area highlighted in yellow includes the paper-based microfluidic device and a glass trough for particle collection. The UV lamp used for crosslinking is highlighted in purple, and would be located above the trough during operation. **(b, c)** The flow focusing geometry patterned on fluoro-paper A. Scale bar is 1 cm for **(b)** and 5 mm for **(c)**.

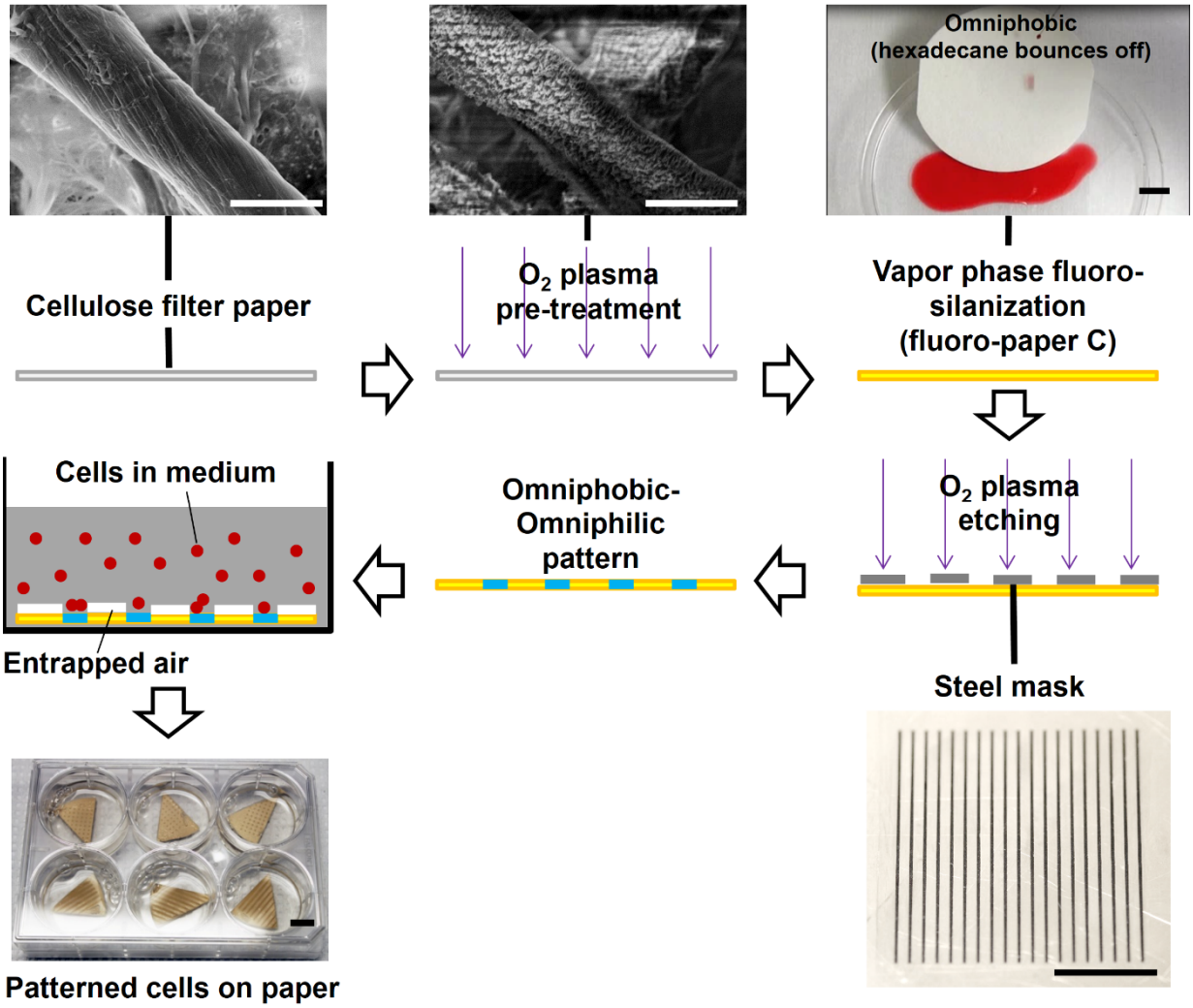

Figure S11. Schematic illustration of the procedure employed to prepare omniphobic fluoro-paper C, omniphobic-omniphilic patterns on this surface, and their use for generating patterned OVCAR3 cell arrays. Scale bars on the SEMs are 10 μm. All other scale bars are 1 cm.

SI References

[1] E. W. Washburn, *Phys. Rev.* **1921** *17*, 273.

Movie Captions

Movie S1. Filling four three-dimensional channels with water, DMF, ethanol, and heptane. Each channel has four bridges on the bottom surface to cross perpendicular channels on the top surface which are also filled with liquid. Water and DMF crossed all four bridges, but ethanol and heptane, due to their high evaporation rates, only crossed the first two bridges out of four. Therefore, ethanol and heptane were also added to the other ends to fill the entire channel.
Movie S2. A printed wettable pattern on fluoro-paper B being filled with dyed silicone oil via capillary action.
Movie S3. Multiplexed heptane-water dispenser device on fluoro-paper A.
Movie S4. Surface emulsification to produce polymer micro-particles on fluoro-paper A.