Electronic Supplementary Information

Rapid Fabrication of Pressure-Driven Microfluidic Devices in Omniphobic R^F Paper

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Materials and Equipment

The cardstock paper and the adhesive tape used to seal the microchannels were purchased from Staples, Inc. (Boston, MA). The double-side adhesive strip (3M Command Medium Picture Hanging Strips) used to attach the flangeless ferrules to the device was purchased from Dickson Brothers (Cambridge MA). The flangeless ferrules that connected the microfluidic device with the tubing were purchased from Upchurch Scientific, (Oak Harbor, WA). Silicone tubing (1.57 mm OD) was obtained from VWR International LLC (Chicago, IL).

3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10, 10–heptadecafluorodecyltrichlorosilane, $CF_3(CF_2)_7CH_2CH_2SiCl_3$ ($C_{10}{}^F$) and decyltrichlorosilane ((C_{10}) were purchased from Gelest Inc (Morrisville, PA). All chemicals were used as received without further purification. The Silhouette Cameo electronic craft cutter (Silhouette Cameo, Silhouette America Inc), cutting tools, and engraving tip were obtained from Silhouette America Inc (Orem, UT).

Device Fabrication

Fig. S1 sketches the method used to fabricate pressure-driven paper microfluidic devices from cardstock paper. We designed the channels using computer-assisted design software (Adobe Illustrator® CS5, Adobe Systems Incorporated.) and used an electronic craft cutting/engraving tool (Silhouette Cameo, Silhouette America Inc.) to carve the design in the cardstock paper substrate (see Fig. S1).

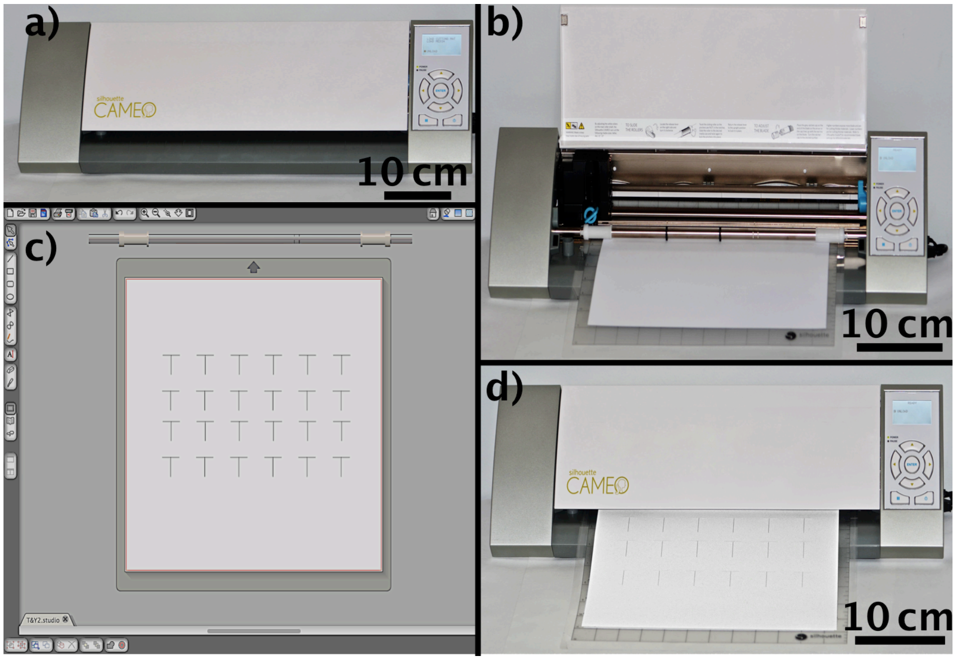

Fig. S1 Silhouette Cameo electronic craft cutting tool a) before loading the paper, b) with the paper loaded. c) The microfluidic device design is generated using the cutter software, d) the craft cutter carves the design into the cardstock paper. The entire process takes less than 40s.

The silanization reaction was conducted in a chamber with a volume of 0.01 m^3 at a temperature set at 95 °C. The silanizing reagent is transferred into a glass vial under inert gas atmosphere and placed inside the chamber together with the samples. Each experiment typically required approximately 100 mg of C_{10}^F in 5 mL of anhydrous toluene. The organosilane was vaporized at 95 °C under reduced pressure (~30 mbar, 0.03 atm) and allowed to react for 5 minutes. Diffusion inside the reaction chamber is sufficient for an even distribution of the organosilane within the chamber.

After the hydrophobic treatment, the top of the channel was sealed with transparent tape (PET/EVA/LDPE, Fellowes adhesive sheet) to generate a flexible microfluidic device with an optically transparent cover. Holes (1 mm diameter) were cut in the tape using the craft-cutting tool to serve as inlets and outlets. Flangeless ferrules (P-200 NX, Upchurch Scientific, Oak Harbor, WA, USA) with 1.59 mm outer diameter (O.D.) were used to connect the inlets and PE tubing with 1.59 mm inner diameter (I.D.) Rings of double-sided strip (3M Command Medium Picture Hanging Strips), were cut using two punch biopsy instruments (1.5 mm and 6 mm Miltex Sterile Disposable Biopsy Punches), and used to affix the ferrules over the holes. Fluid flow was provided by a syringe pump (Harvard Apparatus, PHD 2000) at a flow rate of 10 μL/min, unless otherwise specified.

Cost of Fabrication

Excluding labor and capital expenses, we estimate the cost for making any of the microfluidic devices described in this paper be is less than $0.007 (all prices are for small or research quantities of materials and reagents): i) The estimated cost of the paper is less than $0.0006 (~6 cm^2 at $0.0001 per cm^2 for cardstock paper). ii) The estimated cost of the organosilane is less than $0.00008 per cm^2 (~$2 per gram; we estimate that 40 μL of organosilane can functionalize over one thousand 1 cm^2 devices). iii) The estimated cost of the tape used to seal the device and to affix the ferrules is less than $0.005

(~6 cm^2 at \$0.00083 per cm^2 for the adhesive sheet). The estimated cost for the reusable flangeless ferrules and for the tubing used to connect the microfluidic device to a syringe pump is less than \$3 (two flangeless ferrules at \$1.1 each, 30 cm of PTFE tubing at \$2.45/m).

Device Disposal by Incineration

Devices fabricated using omniphobic paper that become contaminated with biohazardous waste can be incinerated to produce minimal amounts of solid by-products (See Fig S2, ESI†). Please see ref. [23] for a discussion of the environmental impact of burning R^F paper.

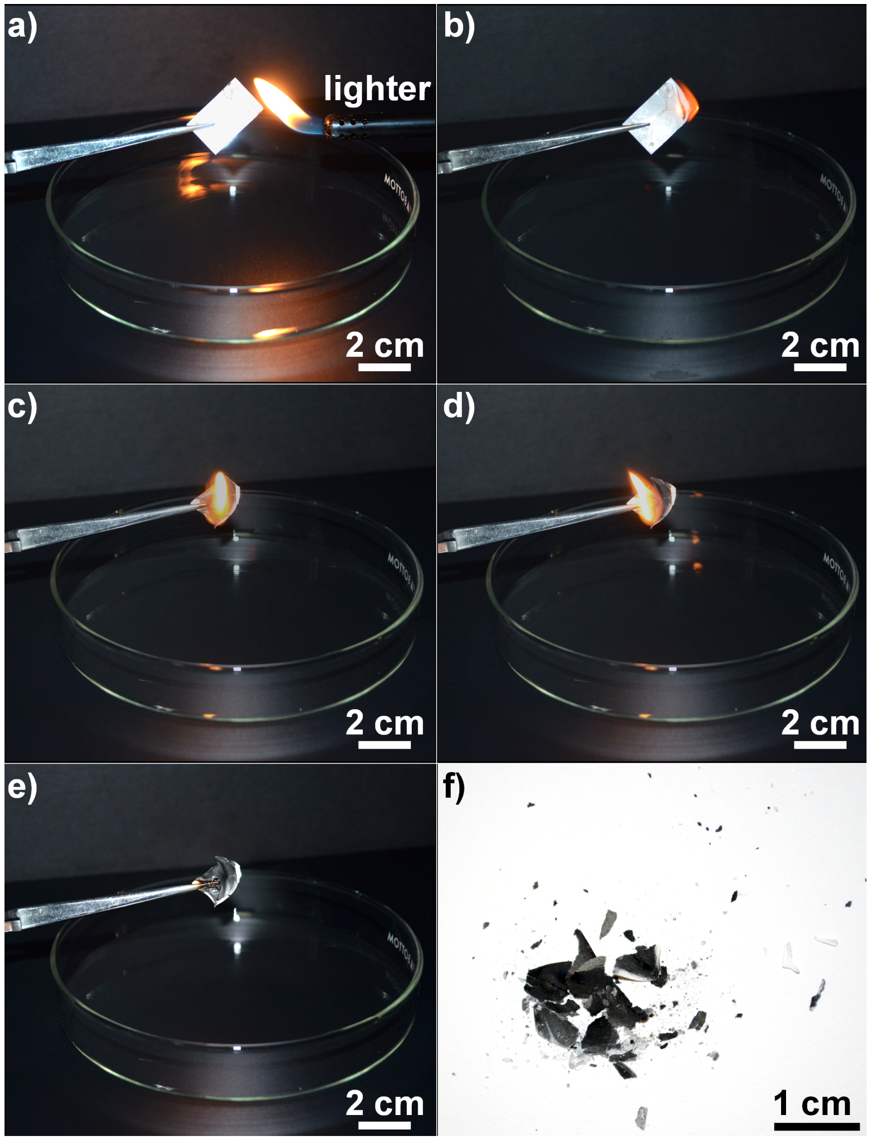

Fig. S2 Demonstration of burning a device assembled from a layer of omniphobic paper, functionalized with C_{10}^{F}, and tape (PET/EVA/LDPE).

Distribution in the of sizes of the droplets

We used ImageJ (http://rsbweb.nih.gov/ij/) to measure the size of 20 consecutive droplets generated at three different rates, and calculated the standard deviation (σ) and the mean (μ) diameter of the drops at each flow rate. The coefficient of variation (CV) was calculated as σ/μ. CV values in percentage were 6.2%, 1.6% and 1.1% for droplets rates 1.25, 0.8, 0.5 Hz, respectively. Rates ranging from 1.25 to 10 Hz exhibit similar CV values.

Scanning Electron Microscopy

The scanning electron microscope (SEM) images (insets in Fig. 2C, D, Fig. S3A, Fig. S7) of the paper microfluidic device were acquired with a Zeiss Supra55 VP FESEM at 2 kV at a working distance of 6 mm. Before SEM imaging, the sample was sputter coated with Pt/Pd at 60 mA for 15–45 s.

Contact Angle Measurements

The contact angle measurements were performed by a contact angle goniometer (Ramé-Hart model 100, Ramé-Hart Instrument Co.) at room temperature (20 – 25 ^{o}C) with ~20% relative humidity. The droplet volume for the measurement was ~10 μL (unless otherwise specified).

Porosity

In order to estimate the porosity (void fraction) of the paper substrates we used an analysis method based on image processing. SEM images of the cross-sections of paper were binarised and porosity was calculated as the black to white ratio (Fig. S3). The average porosity of cardstock paper was $\varepsilon = 0.34 \pm 0.02$.

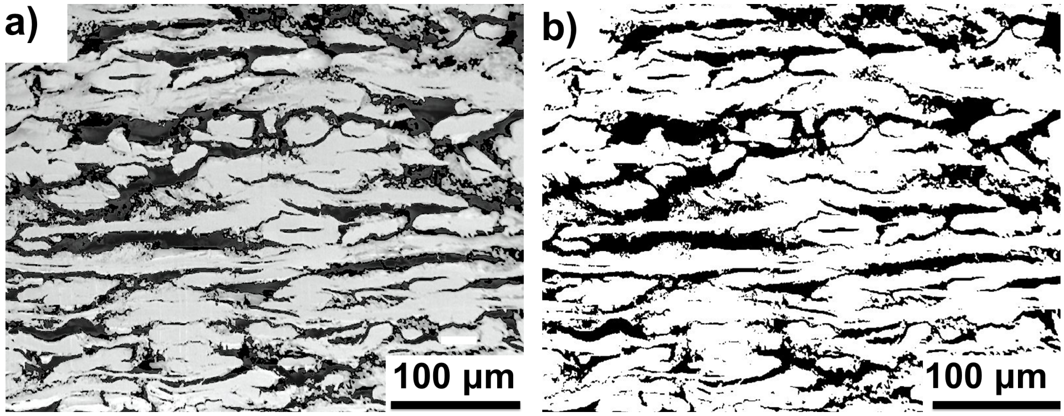

Fig. S3 SEM image (left) and binarised image (right) of a cross section in cardstock paper.

Supplemental Table 1: Porous valves for water. The table shows the pressure difference required to move water through the pores in paper across a distance *L* between two open channels, where *t* is the time required for the liquid to cross that distance, *P* is the pressure drop, μ is the viscosity of the liquid (Pa·s), and *k* is the permeability of the medium (m^2).

***P* (Pa)**	***L* (m)**	***t* (s)**	**Error (n=4)**	**μ (Pa·s)**	***k* (m^2)**
4.0E+04	1E-03	1.5	±0.5	8.90E-04	1.48E-14
4.0E+04	2E-03	5	±1.0	8.90E-04	1.78E-14
4.0E+04	5E-03	22	±3.0	8.90E-04	2.53E-14

Effective Diffusion Constants of NH_3 and HCl through voids in omniphobic paper

The diffusion constant of NH_3 in air, D_{bulk}, has an experimental value of 2.2 x×10^{-5} m^2/s at 25° C/1 atm.[1] Similarly, the diffusion constant of HCl in air is D_{bulk}=1.8x10^{-5} m^2/s.[2] The effective diffusion constant of gases in porous media D_{eff}, can be estimated using the Bruggeman's correction[3] for the porosity ε :

$$D_{eff} = \varepsilon^{1.5} D_{bulk} \tag{1}$$

Since ε ~ 0.3, the effective diffusion constants of NH_3 and HCl through cardstock paper are on the order of 10^{-6} m^2/s.

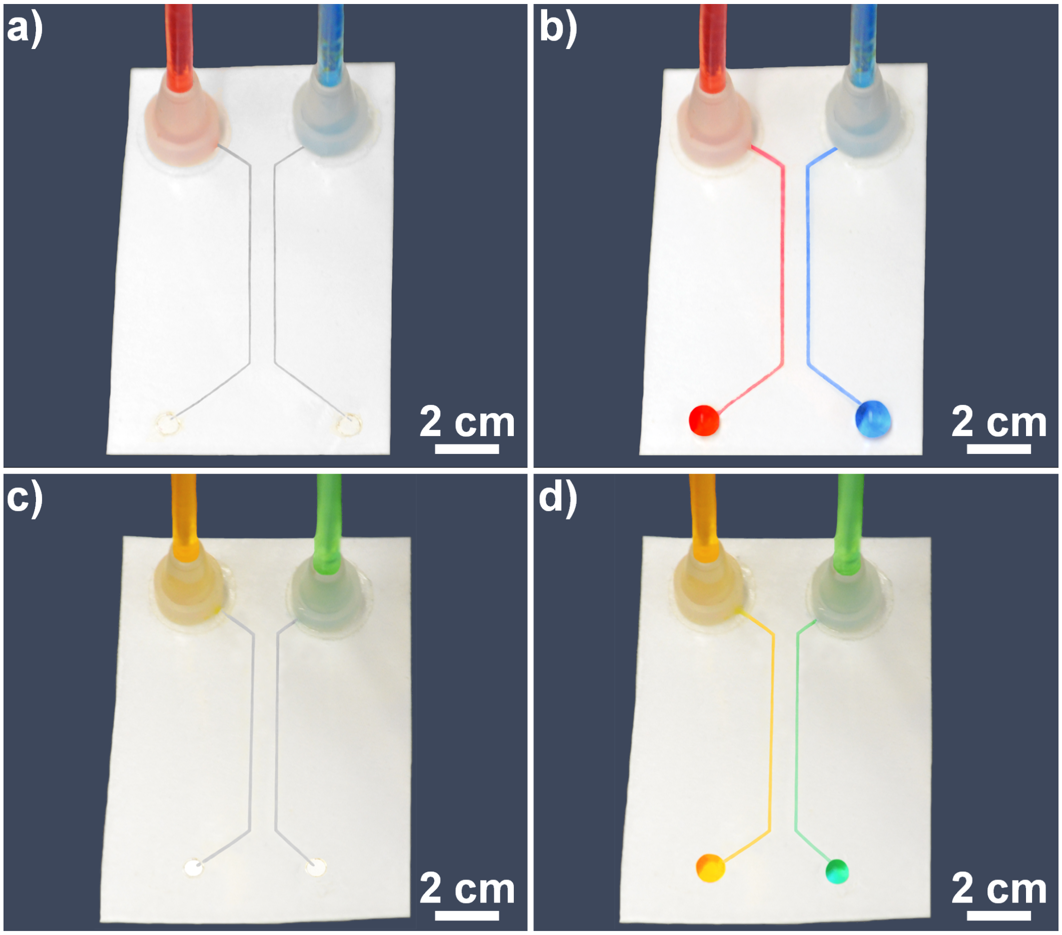

Fig. S4 A universal indicator in a channel parallel to a solution of a non-volatile acid or base does not change color. b) Streams of 38% $H_2SO_{4\ (aq)}$ and 0.05% universal pH indicator are introduced in channels A and B, respectively. Similarly, streams of d) 8.33% NaOH, which has the same pH=13.6 as a 28% solution and 0.05% universal pH indicator were introduced in channels A and B, respectively. No transfer of liquids occurs between parallel channels 1 mm apart.

Supplemental Table 2: Oxygen permeability for several materials used to fabricate microfluidic devices (adapted from [4,5])

Material	Oxygen Permeability · 10^9 cm^3 (STP)· cm/s ·cmHg
Whatman#50	8000
PDMS	60
Polyethylene(low density)	0.8
Polyvinyl chloride	0.14
Nylon 6	0.004
Mylar	0.0019
Teflon	0.0004

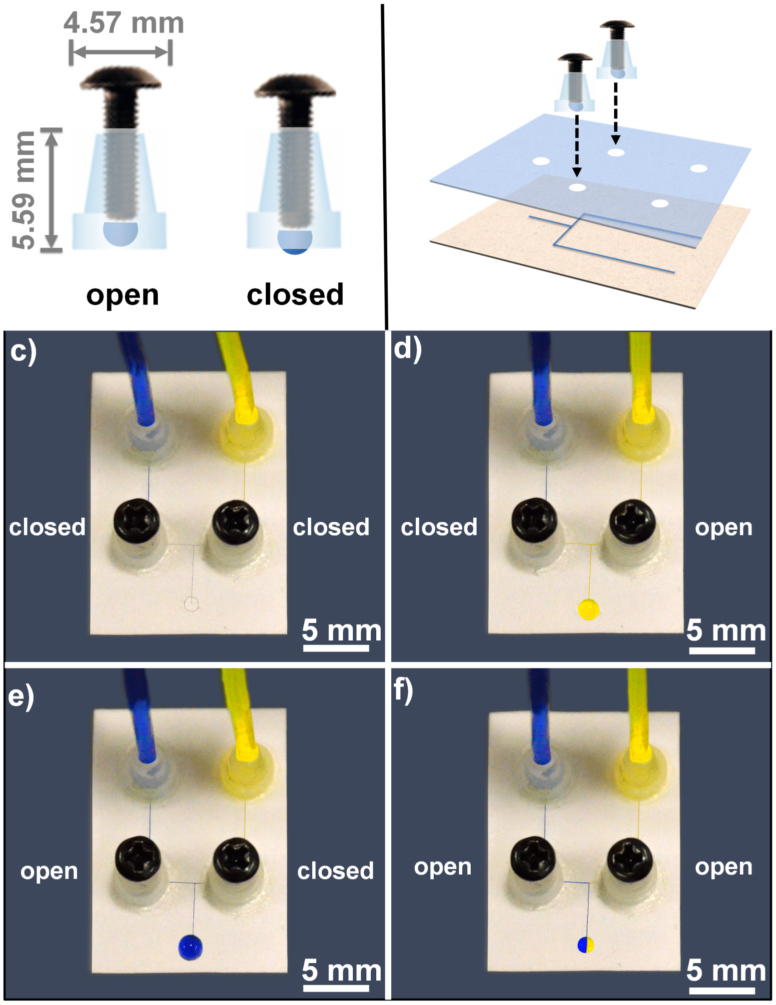

Fig. S5 a) Design of the “twist” valve. b) Fabrication of a microfluidic system incorporating the valve. We fabricated twist valves from flangeless ferules and small machine screws, with a small amount of PDMS (~10 μL) added to the bottom part of the screw and allowed to cure to form a soft “cushion”. When turned clockwise, the screw lowers into the channel and contacts the bottom of the channel through the PDMS cushion. Turning the screw counterclockwise removes the obstruction and opens the valve. c) Demonstration of fluid flow in a device with both valves closed. d) Demonstration of fluid flow in a device with left valve closed, right valve open. e) Demonstration of fluid flow in a device with right valve closed, left valve open. f) Demonstration of fluid flow in a device with both valves open. The last segment of the channel exhibits laminar flow.

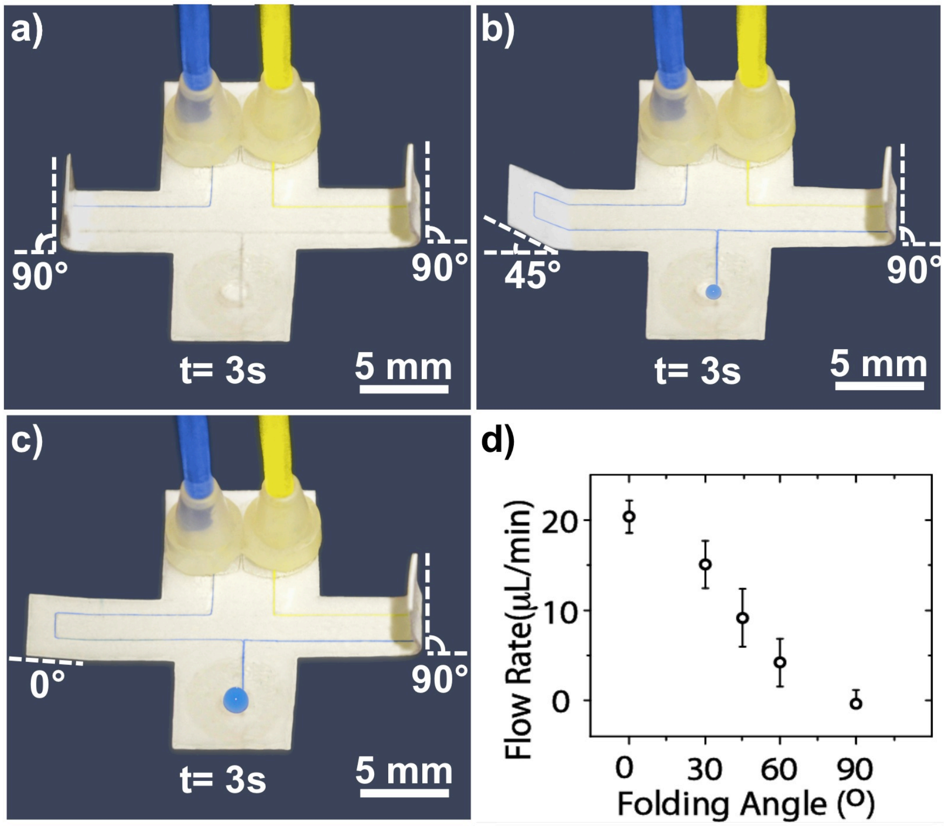

Fig. S6 Flow rate as a function of the dihedral angle of the "folding" valves. The flow rate was measured as the folding angle was adjusted for the left channel. The folding angle for the right channel was maintained at 90° throughout the experiments. The sequence of images of the device shows the left valve at different angles of folding: a) 90°, b) 45°, c) 0°. After t=3 s, drops of different sizes, corresponding to different levels of channel obstruction by the "fold" valve, are expelled from the outlet. d) Dependence of the flow rate on the folding angle.

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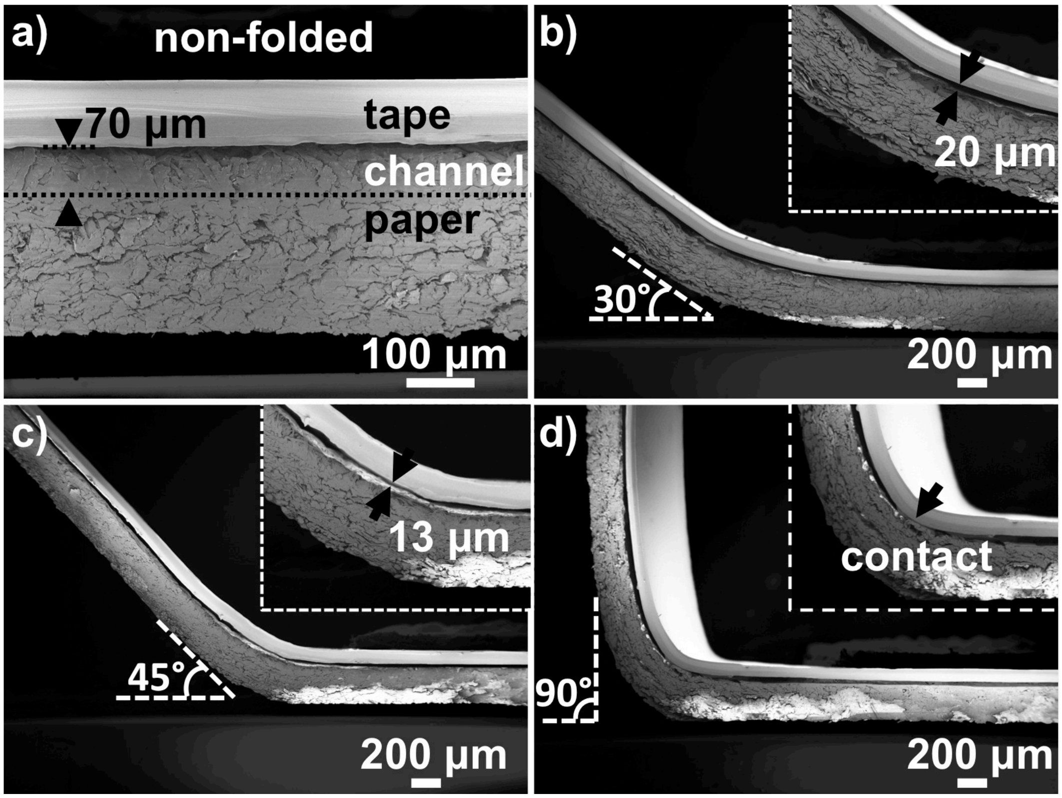

Fig. S7 SEM images of transverse sections through the "fold" valves, showing the constriction of the channel as a function of the folding angle at the valve. The sequence of images of the device shows the left valve at different angles of folding: a) 0°, b) 30°, c) 45°, d) 90°. At folding angles of 30° and 45°, the channel height appears to be lower than before folding (0°). At 90°, the channel top and bottom appear to be in close contact (height of channel less than 3µm).

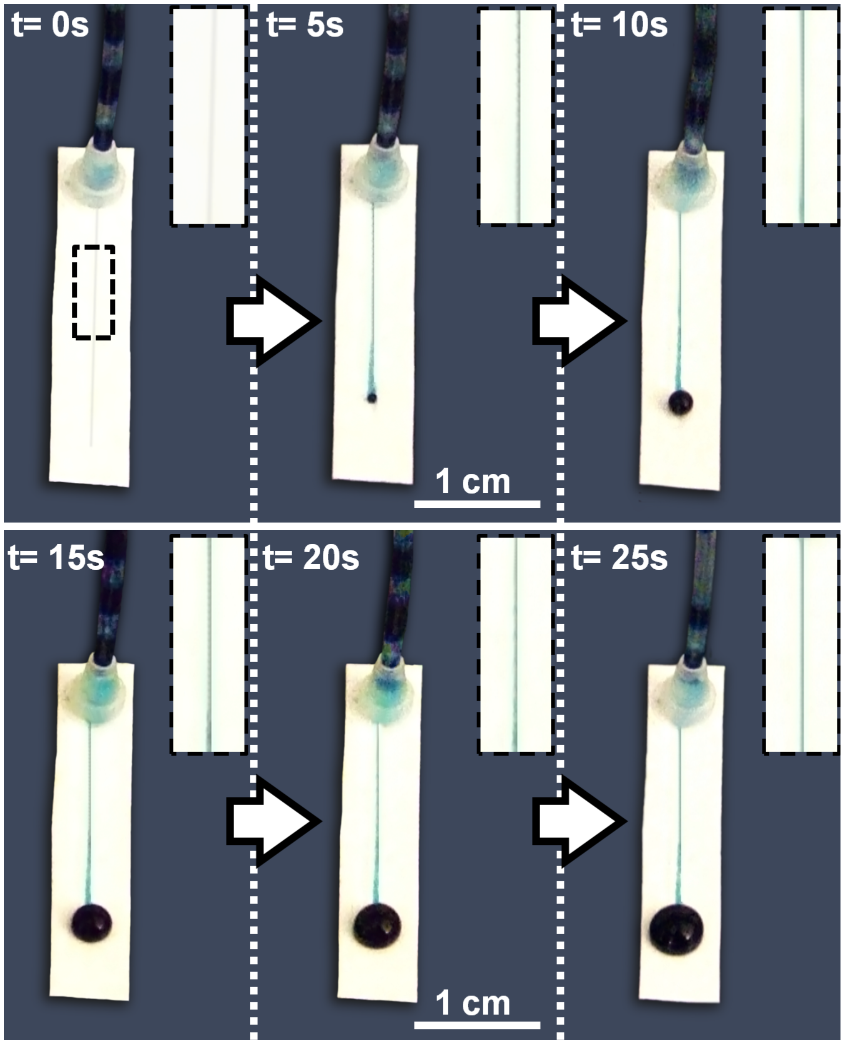

Fig. S8 Snapshots of the series of plugs of an aqueous solution of blue dye separated by air bubbles as they pass through the open channel in hydrophobic paper. Air is expelled through the paper membrane, as observed at a flow rate of 25 μL/s. Bubbles are not visible in the microfluidic channel as they rapidly diffuse through the walls of the device. The flow of the aqueous phase in the channel is uninterrupted.

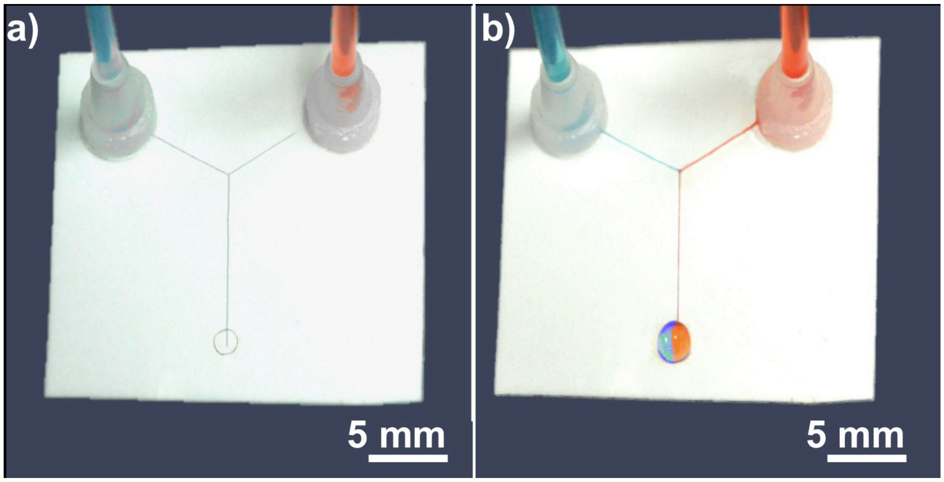

Fig. S9 A Y-shaped microfluidic channel (47 µm wide, 138 µm deep) exhibits laminar flow with diffusion-limited mixing of two aqueous solutions of dye. In this experiment, after the channels are carved into the cardstock paper using a thin cutting blade, the paper is functionalized using decyltrichlorosilane (C_{10}^{H}) to render it highly hydrophobic.

References:

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