

Supplemental Information

Materials

Tetraethoxysilane (TEOS), methyltrimethoxysilane (MTES), *N*-[3-(Trimethoxysilyl)propyl] ethylene diamine, toluene and ethanol were purchased from Sigma Aldrich. Poly(dimethylsiloxane) (Sylgard 184 Silicone Elastomer Kit) was purchased from Dow Corning. All chemicals were used as received.

Coating precursor mixture preparation

The coating precursor mixture is prepared by combining TEOS, ethanol, and pH 2 H₂O (adjusted with HCl), for the Rhodamine B test, or TEOS, MTES, ethanol, and pH 4.5 H₂O for all other tests. The precursor mixture containing MTES¹ produces coatings with fewer cracks and is very resilient to toluene. Both mixtures are initially immiscible. They are therefore heated in a microwave for 3 s for 5-10 iterations after which they become homogenous solutions. The mixtures are then allowed to react at room temperature for 24 hrs or in an oven at 65 °C for 12 hrs before they are used.

Channel coating procedure

The channels are produced using the principles of soft lithography^{2,3}. The channels are oxygen plasma treated and bonded to a glass slide. Soon thereafter, they are filled with the precursor mixture. They are then placed on a 105 °C hotplate for 10 s. The mixture is then blown out with air before it has solidified, leaving behind a viscous coating on the channel walls. While still on the hotplate, 10 mL of air is cycled through the channels to evaporate the remaining solvent and convert the coating into a glass layer.

Rhodamine B test

Two PDMS channels are used for this experiment. They are straight, 2 cm in length, and have cross-sectional dimensions of 50 by 35 μm. One of the channels is coated using the TEOS, ethanol, pH 2 water precursor mixture. The other is left uncoated. Rhodamine B solution is prepared by dissolving Rhodamine B in distilled water to produce a 50 μM aqueous Rhodamine B solution. Both the coated and uncoated channels are then filled with the aqueous Rhodamine B solution. They are then stored in a dark drawer for 4 days over which time the water evaporates leaving behind precipitated Rhodamine B. The channels are then imaged using a CCD camera (QICam, QImaging) mounted on an inverted fluorescent microscope (Leica model DM IRB). The exposure time is 0.2 s and the gain is 1. These settings are the same for both images. The images are shown cropped and aligned in their raw form in Fig. 2.

Toluene test

Two PDMS channels are used for this experiment. They are straight, 2 cm in length, and have cross-sectional dimensions of 50 by 35 μm. One channel is coated using the TEOS, MTES, ethanol, pH 4.5 water precursor mixture. The other is left uncoated. Toluene is then pumped through both channels at 100 μL/hr using syringe pumps (Harvard PHD2000).

Toluene-in-Water and Water-in-Toluene droplet generation

Two flow-focus drop-makers are prepared. Both are coated with the TEOS, MTES, ethanol, pH 4.5 water precursor mixture using the same treatment procedure as described above except that the time on the hotplate is shortened to 5 s before the mixture is blown out with air. This deposits a thinner layer of sol-gel glass that more effectively coats the narrow 20 μm nozzle of the drop-maker. The coating precursor mixture is injected and blown out of the channels through the disperse phase inlet is. We have also coated the channels by flowing the precursor solution into both the continuous and disperse phase inlets simultaneously. However, this does not seem to be necessary.

The coated channels are then functionalized to have the necessary wetting characteristics. To make the channels hydrophilic to produce toluene-in-water emulsions, the channels are treated with a preconverted mixture N-[3-(Trimethoxysilyl)propyl] ethylene diamine, ethanol, and pH 2 water adjusted with HCl in a 1:1:1 volumetric ratio. The channels are filled with the mixture and allowed to sit for 5 min. Then the mixture is blown out with air. This makes the device sufficiently hydrophilic to produce toluene-in-water emulsions, Fig. 4b.

To make the channels hydrophobic we treat them with Aquapel®, an inexpensive auto-glass treatment that makes the channels hydrophobic. The channels are filled with Aquapel®, allowed to sit for 5 min, and then the Aquapel® is blown out with air. This makes the device sufficiently hydrophobic to produce water-in-toluene emulsions, Fig. 4a.

References

1. S. Z. Yu, T. K. S. Wong, X. Hu and K. Pita, *Journal of the Electrochemical Society*, 2003, **150**, F116-F121.
2. D. C. Duffy, J. C. McDonald, O. J. A. Schueller and G. M. Whitesides, *Analytical Chemistry*, 1998, **70**, 4974-4984.
3. G. M. Whitesides, *Nature*, 2006, **442**, 368-373.