

Patterning microfluidic device wettability using flow confinement

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Supplemental Information

This supplemental information contains details for fabricating microfluidic devices to make double emulsions. It is organized into three sections: device design, fabrication, and wettability patterning. In the wettability patterning section, we provide two surface modification reactions, UV-initiated and thermal-initiated reactions. Both methods are simple and robust, and we hope that by providing two options, more people will try the method out. If you have additional questions, feel free to send an email to aabate@post.harvard.edu.

Device design

We fabricate our devices using photolithography. An essential part of this process is a photomask containing a picture of the device to be fabricated. To make the photomask, we draw a to-scale schematic of the device in AutoCAD, and send it to Cad Art Services, Inc., Bandon, OR, USA for printing. Cad Art prints the picture on transparency plastic in UV-absorbent ink. An inverse image of the device is shown in Fig. S1. To inject fluids into the device, we require inlet ports that can be interfaced with tubing. We punch holes in the device (Harris Unicore 0.75 mm biopsy punch) that intersect with the microchannels. The holes must be punched accurately, or they will miss the microchannels; to ensure accurate punching, we use an optical guide to make the punch location easier to see. We surround the punch location with polygons that scatter light, making it easy to see. We also provide a large target for the punch by creating a wide basin channel at the punch location. This ensures that even if the punch is slightly miss-aligned, there will still be an intersection with the channel. Below the punch basin is a filter consisting of an array of rhombic posts, as shown in Fig. S1. The gaps between the posts are made narrower than the narrowest constriction on the device, allowing it to filter debris that could lead to clogging.

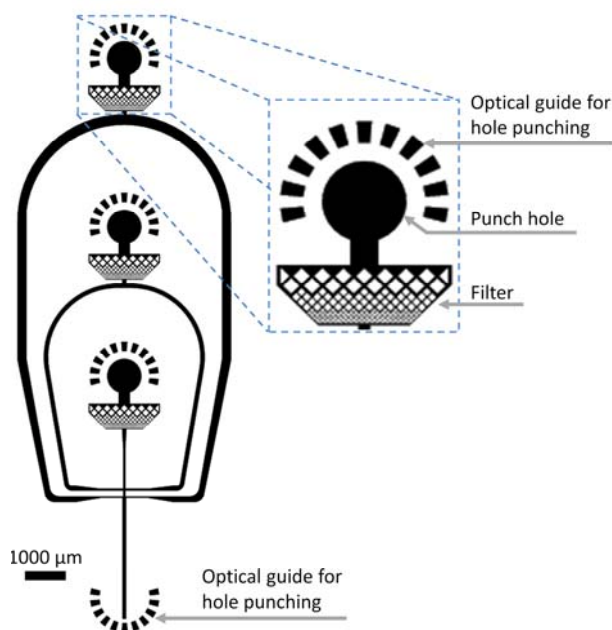


Fig. S1 Inverse grayscale image of AutoCAD drawing of the microfluidic device used to create double emulsions. Depending on how the wettability of the device is patterned, it can form O/W/O or W/O/W double emulsions. The device has three inlets and an outlet, which must be punched manually to interface with fluids. The punch locations are surrounded by rectangular posts that scatter light, making it easier to see where to punch. Below each punch is a filter that prevents debris from entering the device.

Coating PDMS devices with sol-gel

To control the wettability of our devices we coat them with sol-gel. To prepare the sol-gel solution we combine 1 mL tetraethylorthosilicate (TEOS), 1 mL methyltriethoxysilane (MTES), 0.5 mL (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-triethoxysilane, 2 mL trifluoroethanol and 1 mL 3-(trimethoxysilyl)-propylmethacrylate; the solution should be yellow and clear, and can be stored for up to a week at 2 - 8° C. Before the coating can be applied the sol-gel must be preconverted by adding an acid catalyst. To preconvert, we combine 0.5 mL of the sol-gel solution, 0.9 mL methanol, 0.9 mL trifluoroethanol, and 0.1 mL HCl aqueous pH 2. After the catalyst is added the solution may turn cloudy; it is vigorously shaken for several seconds and placed on a hot plate set to 85° C for 30 s; this is repeated until the reaction mixture clears, which takes approximately 2 minutes. The solution is loaded into a 1 mL plastic syringe with a 27 G needle. The amount of trifluoroethanol and methanol added can be varied, to control the coating thickness; by adding more of these solvents, thinner coatings are produced because the sol-gel is more dilute. The dilution should be chosen to match the dimensions of the channels: the smaller the channels, the thinner the coating must be and, thus, the higher the dilution. The dilution we describe is appropriate for channels about 100 μm in diameter, the dimensions of our device. We have found that the sol-gel can be diluted by as much ten times, without adversely affecting wettability control.

The device must be coated immediately after plasma bonding. A 1 cm piece of poly(ethylene) (PE) tubing is inserted into the outlet of the device. The device is then filled with the preconverted sol-gel mixture via the tubing. The device is then placed on a hotplate set to 180° C, and held down with tweezers to ensure good thermal contact. After a few seconds a popping sound can be heard as the sol-gel mixture vaporizes and the channels are blown clear. At this point, the PE tubing is removed so that it does not melt, but the device is left on the hotplate for additional 60 s to allow the coating to fully cure. The device is then removed from the hotplate and allowed to cool. The coated device can be stored for several months wrapped in aluminum foil, before patterning wettability. This process describes coating a single drop maker; however, normally our devices consist of between 5-10 drop makers, all on the same chip. The coating process is the same, except that many devices are coated in parallel.

Patterning microfluidic device wettability with flow confinement

Flow confinement can be used to pattern wettability using a variety of surface modifying reactions. Here, we describe two reactions, both polymerization reactions, one initiated by UV light and the other by heat.

UV initiation

For the UV-initiated reaction we require a bright UV-light source. We use a home-built microscope outfitted with Koehler illumination as the light source. The lamp of the Koehler illumination can be switched between a fiber-coupled halogen lamp (Thorlabs) and a fiber-coupled 300 W UV-arc lamp (Exfo). With the Koehler focusing optics this setup produces a UV beam on the sample with an optical power 150 mW/cm² at a wavelength of 365 nm. This setup also allows us to see the sample during the exposure. We set the device up and start the flows using the halogen lamp, and then, when everything is aligned and flowing steadily, start the exposure by switching to the UV lamp. We continue to watch the sample during the exposure, to monitor polymerization and adjust flow rates as needed. This, admittedly, is a somewhat specialized piece of equipment, although it only cost approximately \$5,000 to build: \$3,000 for the UV lamp and \$2,000 for the halogen lamp, objectives (Mitutoyo), and optics (Thorlabs). Alternatively, the exposure could also be done using a standard fluorescence microscope with a UV source. In this case, an appropriate filter set must be inserted into the filter cube of the microscope, to expose the sample to UV light. Another option would be to use a flood UV system or black light with the correct wavelengths; however, a drawback to this approach is that, without a microscope, it will not be possible to see the polymerization as it is progressing. Another drawback is that it is unlikely that such a system will provide high light intensity, so that longer polymerization times will be needed to achieve sufficient grafting.

To prepare the monomer solutions we combine 0.5 mL ethanol, 0.2 mL acrylic acid and 0.1 mL 2-hydroxy-2-methylpropiophenone (Darocur® 1173). The solution is loaded into a 1 mL syringe (Hamilton Gas Tight). A 3 mL plastic syringe is filled with de-ionized water for the blocker phase. The water syringe is connected to the microfluidic device and used to flush trapped air from the channels. The monomer solution is then connected to the device, along with an additional piece of PE tubing to the continuous phase inlet, which serves as the outlet during the patterning process. The remaining fourth inlet is plugged with a melted small piece of PE tubing. Using bright field illumination, the device is aligned with the light source and the syringe pumps are started at 200 $\mu\text{L}/\text{h}$ for the monomer solution and 2000 $\mu\text{L}/\text{h}$ for the inert solution. Once the flows are stable, the light source is switched to the UV lamp to initiate polymerization. As polymerization proceeds, the viscosity of the monomer solution increases; to maintain the interface at the correct location, we increase the flow rate of the water phase in 300 $\mu\text{L}/\text{h}$ steps and reduce the flow rate of the monomer in 10 $\mu\text{L}/\text{h}$ steps approximately every 30 seconds. After 6 minutes the UV light is switched off. With the inert phase still running, the monomer tubing is pulled out of the device; this flushes the device with the inert phase, removing unreacted monomer.

There are two benefits to using bulk initiators rather than surface-immobilized initiators for the polymerization. Unlike with an immobilized strategy in which there are a finite number of initiators on the surface, in a bulk strategy there are essentially a limitless number of initiators; as the reaction progresses and initiators are consumed, new initiators are introduced by the flow. This enables the reaction to run as short or as long as desired, to control the amount of polymer grafted. Another advantage is that there are a larger variety of bulk initiators available for purchase than initiators that can be bonded to the surface. This affords greater flexibility when choosing the initiators and the linkage chemistry, which may be important for certain applications.

Thermal initiation

To pattern wettability using a thermal-initiated polymerization reaction, all that is required is a hotplate. We also use a reflection microscope, to visualize the polymerization. We prepare the monomer solution for this reaction by combining 500 μL de-ionized water, 200 μL acrylic acid, 100 μL of a freshly prepared solution of APS in water (10 wt %) and 16 μL tetramethylethylenediamine (TEMED). The monomer solution is loaded into a 1 mL syringe (Hamilton Gas Tight) and cooled with an ice package. A 3 mL plastic syringe is filled with glycerol, which will act as the blocker phase. The glycerol syringe is connected to the device, and the device is flushed to remove trapped air. After connecting the monomer solution, an additional piece of PE tubing is connected to the continuous phase, to serve as the outlet during the patterning process. Again, the remaining fourth inlet is plugged with a melted small piece of PE tubing. Using the reflection microscope, the device is aligned on the hotplate and the syringe pumps are started at 200 $\mu\text{L}/\text{h}$ for the monomer solution and 2000 $\mu\text{L}/\text{h}$ for the inert solution. Once the flows are stable and a sharp interface has formed in the junction, the hotplate is set to 80° C. As the temperature rises above 75° C, a significant increase in the viscosity of the monomer solution occurs. To maintain the interface in the

center of the junction, the flow rate of glycerol is increased in 500 $\mu\text{L}/\text{h}$ steps and the flow rate of monomer is reduced in 10 $\mu\text{L}/\text{h}$ steps approximately every 30 s. After 6 minutes, the hot plate is switched off and the device is removed. To remove remaining unreacted monomer solution and glycerol, the device is flushed with de-ionized water for several minutes.

Other injection strategies for complex devices

Our method can be used to pattern complex devices, including many drop makers connected together; however, there are other devices that are not as easily patterned. For example, to create W/O/W/O triple emulsions requires a device consisting of three flow-focus junctions in series, with a wettability pattern in which the first drop maker is hydrophobic, the second hydrophilic, and the third hydrophobic. This pattern cannot be easily created using flow-confinement as we present it in the communication. However, with simple modifications to the method, this pattern can also be created. The challenge is to make the central junction hydrophilic while leaving the upper and lower junctions hydrophobic; however, to functionalize the central junction, the reactive solution must be flowed past the upper or lower junction, resulting in the patterns hydrophilic/hydrophilic/hydrophobic, or hydrophobic/hydrophilic/hydrophilic, neither of which is suitable for forming triple emulsions. A simple solution is to add a channel to the central junction, to allow the reactive solution to be injected directly, bypassing the other junctions. Another option is to use a “forward-flow” approach, in which all fluids are injected into the inlets of the device and exit through the outlet. If the fluids are injected in the configuration inert/reactive/inert, this will produce the correct pattern to form the triple emulsions; however, a difference with this injection strategy is that the crossover lines will be v-shaped rather than flat.