Patterning microfluidic device wettability using flow confinement†

Adam R. Abate,‡[a] Julian Thiele,‡[ab] Marie Weinhart[c] and David A. Weitz*[a]

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We present a simple method to spatially pattern the surface properties of microfluidic devices using flow confinement. Our technique allows surface patterning with micron-scale resolution. To demonstrate its effectiveness, we use it to pattern wettability to form W/O/W and O/W/O double emulsions.

Many applications of microfluidic devices require channels with patterned surface properties.[1] One such application is the formation of multiple emulsions which consist of large drops with smaller drops inside.[2–4] To make these structures requires microfluidic devices with spatially patterned wettability; this allows the inner drops to be formed in one part of the device and the outer drops in another part.[5–7] However, current methods to spatially pattern the wettability of microfluidic devices are difficult to use and of limited versatility. The best approach for patterning wettability uses a polymerization reaction that is initiated by exposure to ultraviolet (UV) light.[8–11] To spatially control wettability, the microfluidic device is exposed to a spatially controlled light pattern, imparting a wettability pattern of the same shape. However, since micron-scale resolution is required, sophisticated optics and a powerful UV-light source are needed. Moreover, this method is difficult to use to fabricate many devices with the same pattern, since this requires precise alignment of the optical pattern with all devices simultaneously, a technically challenging procedure. A superior wettability patterning approach would combine simplicity with high-resolution patterning, and would allow fabrication of large numbers of devices with identical properties.

In this paper, we present a versatile method for patterning surface wettability. We use an inert fluid to physically confine a chemical treatment that alters wettability in selected regions of the device; this requires only basic equipment and allows high-resolution wettability patterning. Moreover, since spatial control is achieved by physical confinement of the reaction, this approach is versatile, allowing many different surface treatments to be used.[12,13] To illustrate this, we use photo-initiated and thermal-initiated surface treatments with our method. To demonstrate the effectiveness of our approach, we use it to pattern the wettability of microfluidic devices to form both W/O/W and O/W/O double emulsions.

We fabricate our microfluidic devices using soft-lithography in polydimethylsiloxane (PDMS).[14,15] Our devices consist of microchannels 100 μm in height. To control the wettability of our devices, we use a sol–gel coating approach.[9,16] We design a sol–gel coating that is intrinsically hydrophobic, but can be converted to hydrophilic after a chemical treatment. To accomplish this, we incorporate fluorosilanes and methacrylate-silanes into the 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)propyl methacrylate. Before the coating can be applied the sol–gel must be preconverted by adding an acid catalyst. We combine 0.5 mL of the sol–gel solution, 0.9 mL methanol, 0.9 mL trifluoroethanol, and 0.1 mL aqueous HCl, 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 mixture clears, which takes approximately 2 minutes. To coat the channels, we fill them with the sol–gel mixture immediately after plasma bonding. We then heat the device on a hot plate set to 180 °C; this vaporizes the mixture, depositing a uniform sol–gel coating on the channel walls. The coating thickness can be reduced by diluting the sol–gel mixture several times in methanol, without adversely affecting wettability control. Due to the fluorosilanes in the sol–gel, the coated channels are very hydrophobic. To confirm this wettability, we perform contact angle measurements of sol–gel coated glass slides with water drops in air. On a sol–gel coated glass slide the water drop beads up, achieving a hydrophobic contact angle of ∼105°, as shown in Fig. 1A. To switch the wettability to hydrophilic, we use the methacrylate-silanes in the sol–gel. These silanes contain double bonds, which can be used to graft hydrophilic

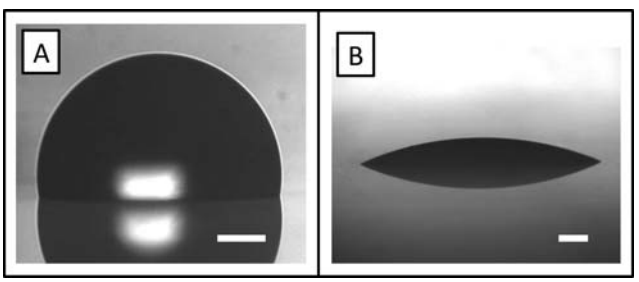

Fig. 1 The sol–gel coating allows us to control the wettability of microfluidic channels. To confirm this, we perform contact angle measurements of sol–gel-coated glass slides with water drops in air. The sol–gel is intrinsically hydrophobic due to the incorporation of fluorosilanes, as confirmed by the hydrophobic contact angle of 105° (A). It is converted to hydrophilic by attaching PAA to the surface using a polymerization reaction, as shown by the hydrophilic contact angle after treatment of 20° (B). The scale bars denote 50 μm.

[a]*School of Engineering and Applied Sciences/Department of Physics, Harvard University, Cambridge, Massachusetts, USA. E-mail: weitz@seas.harvard.edu; Tel: +1 617-495-3275*
[b]*Institute of Physical Chemistry, University of Hamburg, Germany*
[c]*Institute of Chemistry and Biochemistry—Organic Chemistry, Freie Universitaet Berlin, Germany*

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‡ Both authors contributed equally to this work.

polymers to the surface, to make it hydrophilic. For the polymers we use poly(acrylic acid) (PAA) because it has high electrical polarity and is thus very hydrophilic. To graft the PAA, we fill the channels with acrylic acid (AA) monomer solution and initiate polymerization; this creates AA polymers, some of which react with the double bonds on the sol–gel, grafting them to the surface. This switches the wettability to hydrophilic, as confirmed by the hydrophilic contact angle of ~20° on a glass slide treated the same way, as shown in Fig. 1B. With the sol–gel, we can thus control the wettability of our microfluidic devices.[17]

Channel wettability is the most important parameter when forming emulsions in microfluidics, and spatially controlled wettability is essential when forming multiple emulsions. This is because channel wettability determines the type of drops that a microfluidic device forms: if the channels are hydrophobic, water drops in oil are formed, whereas if the channels are hydrophilic, oil drops in water are formed. Thus, a microfluidic device that creates multiple emulsions is a stringent demonstration of the coating technology presented here. To make double emulsions requires a microfluidic device consisting of two drop makers in series; the outlet of the first drop maker feeds into the inlet of the second drop maker, as depicted in Fig. 2A. To make W/O/W double emulsions, the first drop maker is made hydrophobic and the second hydrophilic; this allows the first to make water drops which are encapsulated in oil drops in the second drop maker, as depicted in Fig. 2A. To make a device with this wettability pattern, we use our flow-confinement technique to make the second drop maker hydrophilic. To accomplish this, we inject the reactive monomer solution into the outlet of the device at 200 μL h^{-1} and the inert fluid into the inner-phase and middle-phase inlets at 2000 μL h^{-1}; the

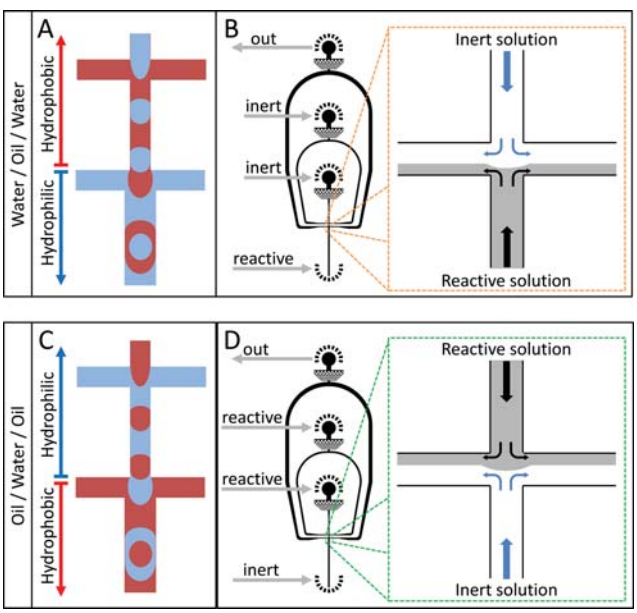

Fig. 2 To form W/O/W double emulsions requires a device in which the upper portion is hydrophobic and the lower portion hydrophilic (A). To create this wettability pattern, we inject a reactive surface treatment solution into the device outlet and an inert blocker solution into the inner and middle-phase inlets (B). Where the two solutions meet a sharp interface forms, due to laminar flow conditions; this sets the cross-over between the treated and un-treated regions. To form O/W/O double emulsions, we invert the pattern (C); this is achieved by switching the inlets into which the reactive and inert solutions are injected (D).

continuous phase inlet is left open, to act as the outlet for both solutions, as indicated in Fig. 2B. This causes the reactive and inert fluids to meet in the second drop maker, so that a stable interface forms between them. The interface is sharp or fuzzy depending on the magnitude of diffusive to advective transport. If diffusion across the interface is small compared to the flow velocity, the reaction is confined to the lower part of the device. This is achieved by controlling the fluid flow rates; this allows us to adjust the Péclet number, which is the ratio of advective to diffusive transport at a fluid–fluid interface. The Péclet number is defined as $Pe = ud/D$, where u is the flow velocity controlled by syringe pumps, $d = 100$ μm the length of the liquid–liquid interface in the drop formation region, and D the diffusion coefficient of the monomer, 1.3×10^{-9} m^2 s^{-1}. We calculate Pe to be ~300; thus, diffusion is negligible in our system, yielding a sharp interface that confines the reaction. This interface sets the location at which the wettability transitions from hydrophobic to hydrophilic. Our technique can also create the inverse wettability pattern, to form O/W/O double emulsions. In this case, we switch the inlets into which we inject the reactive and inert fluids, as shown in Fig. 2C; this makes the first drop maker hydrophilic and the second hydrophobic, as illustrated in Fig. 2D. Other injection strategies can also be used to pattern more complex devices, as discussed in the ESI.†

Since spatial control of the hydrophilic treatment is achieved by physically confining the reaction, our approach is very general with respect to the surface reactions that can be used. To demonstrate this, we use photo-initiated and thermal-initiated polymerization reactions, though many other reactions are possible.[12,13,18] For the photo-initiated reaction, we use a monomer solution consisting of 5.8 mol L^{-1} AA in ethanol. To initiate the reaction, we incorporate 2-hydroxy-2-methylpropiophenone (Darocur® 1173) as a photo-initiator at 22.6 mol%, relative to the amount of AA. Under exposure to UV light, these molecules release radicals that initiate polymerization of the AA. The monomers covalently bond, forming polymers; some of these polymers attach to the double bonds on the surface, attaching them to the surface. The device is exposed to light everywhere, but attachment of the polymers occurs only in the lower portion, because the other regions are blocked by the inert fluid, as shown in Fig. 3A. For the thermal-initiated reaction, we use AA in water at 5.8 mol L^{-1} concentration; however, rather than a photo-initiator we use a thermal initiator. We use APS at 1.50 mol% with TEMED at 3.7 mol% as an accelerant, both in relation to the amount of AA. We inject the solutions as before, but this time initiate the reaction by placing the device on a hot plate set to 80 °C. Again, even though the device is heated everywhere, the reaction is confined to the lower portion of the device by the inert fluid, as shown in Fig. 3B. To verify that this allows us to spatially control grafting of PAA, we image the meniscus between HFE-7500 fluorocarbon oil and deionized water under static conditions in the channel. Due to the different wettability properties in the upper and lower junctions, a meniscus forms between them at the wettability crossover; this allows us to image the shape of the crossover, as shown in Fig. 3C. This confirms that we can spatially control where PAA is grafted.

To demonstrate that flow patterning provides the control needed to form double emulsions, we use it to pattern devices to form both W/O/W and O/W/O double emulsions. As fluids for the double emulsions, we use HFE-7500 fluorocarbon oil with the ammonium salt of Krytox® 157 FSL at 1.8% by weight as the surfactant; for the drops we use deionized water with Pluronic® F127 at 1.0% by weight as the surfactant. To form W/O/W double emulsions, we use flow

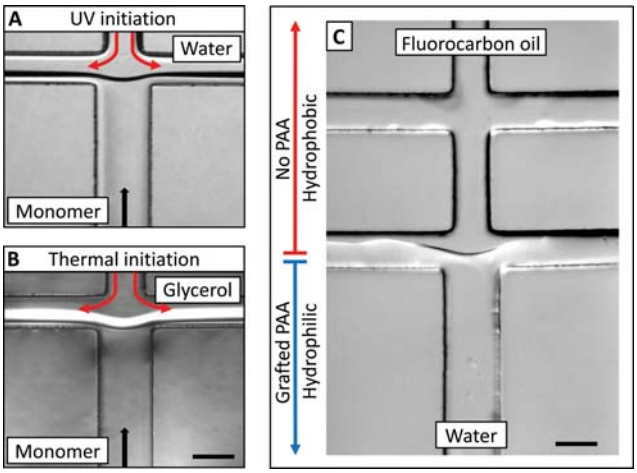

Fig. 3 Since confinement of the surface treatment is achieved by physical means, our approach is general with respect to the surface chemistries that can be used to control wettability, which we demonstrate by using (A) a UV-initiated reaction and (B) a thermal-initiated reaction. Because the same flow pattern is used for both reactions, the resulting wettability patterns are the same. To confirm these patterns, we image the meniscus between HFE-7500 fluorocarbon oil and deionized water under static conditions in the channel. Due to the different wettability properties in the upper and lower junctions, a meniscus forms between them at the wettability crossover; this allows us to image the shape of the crossover, as shown in (C). The scale bars denote 100 μm.

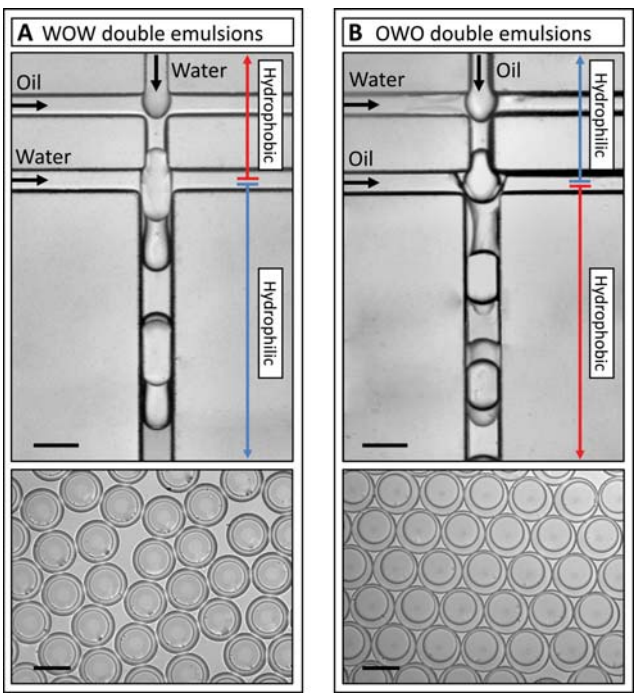

Fig. 4 To form W/O/W double emulsions we use flow confinement to pattern the wettability of a double emulsion device. We make the first drop maker hydrophobic and the second hydrophilic (A). To form O/W/O double emulsions, we invert the pattern (B). To confirm that the double emulsions are formed properly, we image samples collected from both devices, lower panels. The scale bars denote 100 μm.

confinement to make the first drop maker hydrophobic and the second hydrophilic. We inject the fluids into the first, second, and third inlets at 1000, 900 and 1500 μL h^{-1}, respectively; this allows the first drop maker to produce water drops in oil and the second to encapsulate the water drops in larger oil drops, forming W/O/W double emulsions, as shown in Fig. 4A. To produce O/W/O double emulsions, we simply invert the wettability pattern, as shown in Fig. 4B.

Spatial control of wettability is necessary for a variety of applications of microfluidic devices. In contrast to other wettability patterning methods which require precise alignment of an optical pattern with the microfluidic device, our method requires only that fluids are injected in the correct configuration; this makes our approach simple and very scalable. This should be useful for applications that require fabrication of large numbers of devices with identical properties, as needed in scale-up. It should also be useful for patterning the functional properties of devices for biological applications, as in cancer-cell screening applications in which cells must pass through certain regions of the device but be captured by others.[19]

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