Supplemental Data

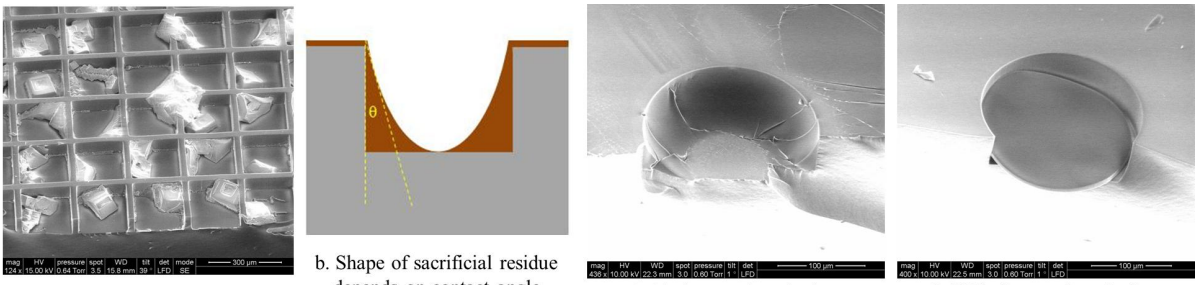
1. The morphology/shape of the coating on the microcavities depends on the type of sacrificial material and the interfacial property.

An amorphous, tightly packed coating is preferred in order to form a tight structural match between the PDMS and sacrificial material phases. Crystal coatings, on the other hand, are not preferred since the crystals are typically extruded from microcavities during the drying process (Fig. S1-a). Examples of crystal coatings are sucrose and inorganic salts. Inorganic salts, such as phosphate saline buffer salts, form crystals on the PDMS microwells (Fig. S1-A). The crystals do not effectively guide wetting due to their discontinuous, non-conformal coating.

Besides the type of sacrificial material, we have found the shape of sacrificial residue deposited in microcavities depends on the interfacial property of the solid surface and sacrificial material solution (Fig. S1-b). An elliptical shape is formed when the solution can wet the solid with small contact angle θ. On the other side, a flat, column shape is formed when the solution cannot wet the solid with a large contact angle θ (in other words, the solution dewets on the solid surface). Here we use PDMS and 25 wt% glucose aqueous solution as the examples for solid surface and sacrificial material solution, respectively.

Native PDMS surface is hydrophobic which tends to trap air bubbles in microcavities. PDMS surface can be oxidized with plasma treatment to modify its surface to be hydrophilic. 25 wt% glucose solution is immediately added to the hydrophilic PDMS surface. Upon drying in air, the glucose coating forms a elliptical shape in microcavities (Fig. S1-c) and can effectively guide wetting. The elliptical shape is caused by the hydrophilic PDMS surface, on which the glucose aqueous solution wets and forms a small contact angle (θ<90°).

When PDMS is not oxidized, glucose forms a flat, column shape in PDMS microcavities (Fig. S1-d). This is caused by the hydrophobic PDMS surface, on which the glucose aqueous solution dewets and forms a large contact angle (θ>90°). This flat, column shape is not effective in guiding wetting in microcavities.



a. 30% PBS salts deposited on oxidized, hydrophilic PDMS

b. Shape of sacrificial residue depends on contact angle during drying in microcavities

c. 25% glucose deposited on oxidized, hydrophilic PDMS

d. 25% glucose deposited on Native, hydrophobic PDMS

Figure S1. *The morphology/shape of coating on the microcavities depends on the type of sacrificial material and the interfacial energy. (a) SEM image showing PBS salts form a discontinuous, non-conformal coating on PDMS microwells (size = 200 μm, depth = 75 μm). (b-c) Shape of the glucose coating in PDMS microwells is dependent on the interfacial properties of the PDMS/glucose solution. (b) Schematic showing the wetting of a glucose solution in a PDMS microwell upon drying. The contact angle θ determines the shape of glucose. (c) An ellipitical-shaped glucose coating is formed on an oxidized, hydrophilic PDMS. (d) A flat, column-shaped glucose coating is formed on a native, hydrophobic PDMS surface.*

2. The coverage of glucose priming in a microwell depends on the glucose concentration.

Assuming the height of the liquid layer above the rim of the microwell is negligible, the total volume of glucose solution loaded into each microwell is:

$$V_1 = \frac{\pi D^2 H}{4} \qquad (1)$$

where D is the diameter of the well and H is its height. During evaporation of the aqueous solvent, the glucose solution does not dewet from the freshly plasma-oxidized, hydrophilic surface, Consequently a conformal coating forms lining the inside of the microwells. If the contour of the glucose layer is regarded as elliptical in shape, the volume of empty space in the well that is not occupied by solid glucose is:

$$V_2 = \frac{\pi D^2 h}{6} \qquad (2)$$

where h is the height of microwell above solid glucose. If the volumetric concentration of glucose is *c*, then

$$cV_1 = V_1 - V_2 \qquad (3)$$

Thus

$$\frac{h}{H} = \frac{3(1-c)}{2} \qquad (4)$$

When $c > 0.33$, then $h < H$, which means the well is fully covered with glucose. When $c < 0.33$, then $h > H$, which means the well is only partially covered with glucose (Fig. S2). The images are consistent with theoretical prediction that the concentration of the glucose solution must be > 33% in order to generate full coverage of the interior surface of the microwells. Based on equation (4), the relative coverage (h/H) is dependent only on the concentration of glucose *c*, not on the dimension of microcavities (D and H). Therefore, the microcavities can be fully primed by using a glucose solution with $c > 33\%$, even for a surface possessing microcavities with a wide range of sizes (10 μm – 3 mm) and depths.

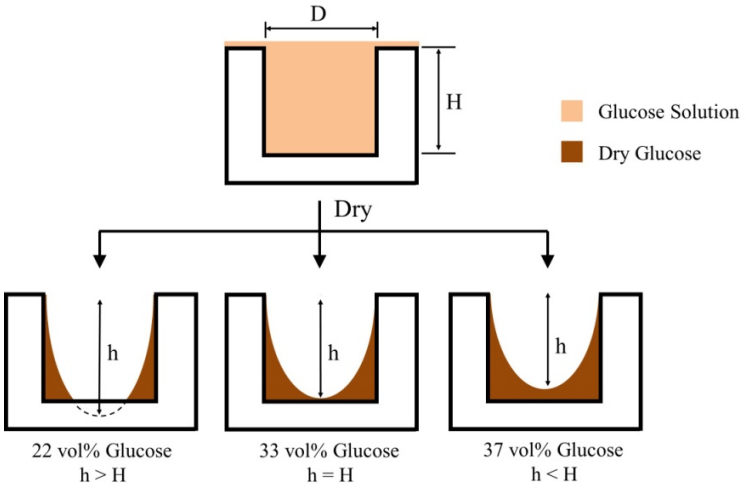


Figure S2. *Schematic showing that the drying of glucose solution in a microwell results in a conformal, elliptical-shaped coating of solid glucose. The degree of coverage depends on the concentration of glucose.*

3. Effect of glucose coating on the hydrophobic recovery of PDMS.

A source of the change in θ is the presence of the glucose coating which creates a hydrophilic surface shielding the water from the PDMS such that the water rapidly wets the surface of the cavity. However, it is possible that the glucose layer also prevents the hydrophobic recovery of the PDMS, thus facilitating the spread of the aqueous solution into the cavity near the edges of the glucose layer. To determine whether a glucose layer could maintain the hydrophilicity of the plasma-treated PDMS surface, the contact angle of PDMS films was evaluated at varying times after priming with glucose. PDMS films were oxidized with plasma and primed with 37% or 0% glucose solutions spread over the surface and dried in air. The films were then stored in air for 0, 2, 5, or 12 days (n = 3 for each condition and time). Immediately prior to measurement of the water-droplet contact angle, the arrays were rinsed with water and dried under a nitrogen stream, and the contact angle was measured. An attenuated total reflectance (ATR)-FTIR spectrometer (Nicolet iS10, Thermo Scientific) was used to confirm the absence of glucose residue on the PDMS surfaces (see below). At day 0, the contact angle for both primed and unprimed PDMS films was 10° ± 5°. By day 2, the contact angle for glucose-primed and unprimed PDMS films was 49° ± 2° and 41° ± 6°, respectively. At day 5, the angle was 56° ± 4° for a primed film and 63° ± 6° for an unprimed film. At day 12, the angle was 65° ± 8° for a primed film and 72° ± 4° for an unprimed film. These results demonstrated that the glucose priming did not delay hydrophobic recovery of the underlying PDMS surface.

4. Measuring the presence of glucose and sorbitol residue on the PDMS surfaces by FTIR.

After wetting, it is desirable to completely remove glucose and sorbitol from the microdevices without residue remaining on the surface. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is a surface-sensitive diagnostic technique which can detect a trance amount of molecules on the top surface (0.5 - 5 μm) of a sample. A flat PDMS sample was oxidized for 2 min and then primed with a thin layer of glucose (37%) or sorbitol (50%). The PDMS sample was dried in air and stored at room temperature for 7 days. The coated PDMS sample was incubated in water for 5 min to dissolve glucose or sorbitol, rinsed with water 5 times, and dried in air. The PDMS sample was then characterized by an ATR-FTIR spectrometer (Nicolet iS10, Thermo Scientific) with a Zinc Selenide (ZnSe) crystal to detect the presence of glucose or sorbitol residue on the PDMS surfaces (Fig. S3). A native PDMS sample was used as a negative control, and glucose and sorbitol were used as positive controls. The characteristic peaks of glucose (1338, 1223, 1199 and 1147 cm^{-1}) and sorbitol (935 cm^{-1}) were absent on coated PDMS samples (after rinsing with water). The spectra of the coated then washed PDMS samples were identical to that of the native PDMS sample. Thus no glucose or sorbitol residue was detectable on the PDMS surface. Since no sugar residue remains on the PDMS surface, glucose and sorbitol are ideal sacrificial materials to guide the wetting of water (or aqueous solution) in microcavities, corners and dead ends.

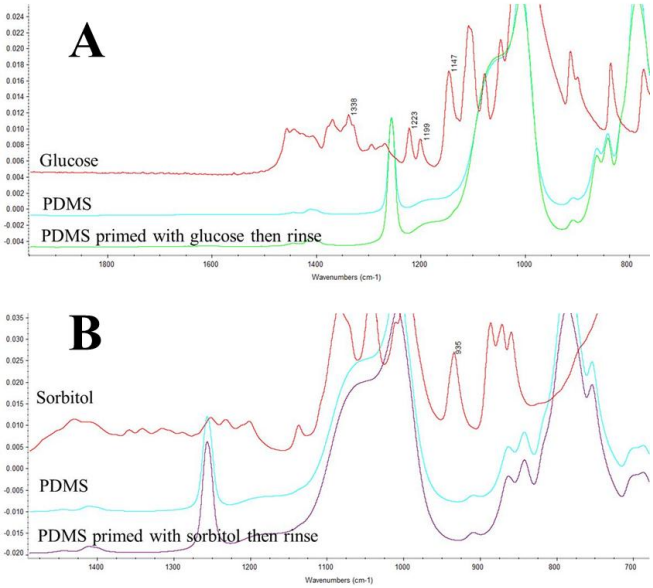


Figure S3. *ATR-FTIR spectra of PDMS samples primed with glucose (A) and sorbitol (B) then rinsed with water. A native PDMS sample was used as a negative control, and glucose and sorbitol were used as positive controls.*

5. Glucose-guided wetting of microwells formed in materials other than PDMS.

Glucose-guided wetting was shown to be effective for PDMS microcavities. Among ten different polymers of interest for microfabrication, PDMS has the most rapid hydrophobic recovery.[2] Therefore, glucose-guided wetting on microwells made in other materials such as polystyrene should be as effective as in PDMS. To demonstrate that glucose-guided wetting is applicable to microwells made from other materials, a microwell array was fabricated from polystyrene.[3] The wells had a diameter of 50 µm and a height of 55 µm. The polystyrene microwell array was oxidized with air plasma for 2 min, primed with a 37 vol% glucose solution in the same way as with microwell arrays formed from PDMS. After priming, a conformal coating of glucose was visible in the microwells (Fig. S4). After storage at room temperature for 7 days, water was added to the polystyrene microwell array. Water quickly (25 s) and completely dissolved the glucose leaving no air bubbles trapped in the microwells (Fig. S4). This result demonstrates that glucose guided wetting is applicable to microdevices made from materials other than PDMS.

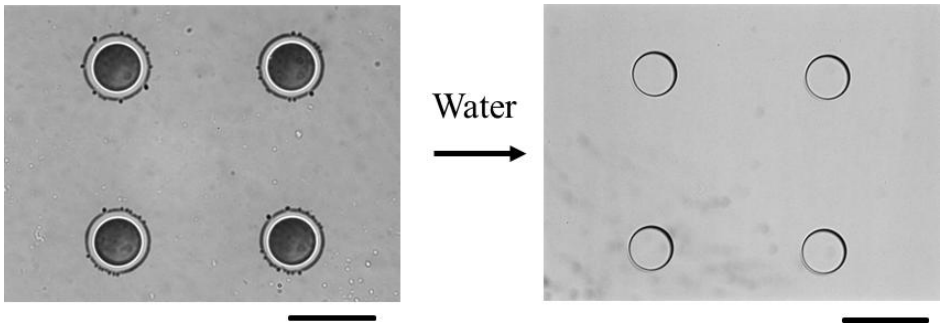


Figure S4. *Transmitted light images showing glucose guided wetting in microwells formed in polystyrene. Scale bar = 100 µm.*

6. Sorbitol guided wetting in microwells

Since glucose is an energy source for microbial metabolism, end users may be concerned about bacterial or fungal contamination during storage, especially in a humid and non-sterile environment. This issue can be addressed by sterilization after the coating is applied using gamma-ray irradiation or ethylene oxide. Sugars that are poor energy sources such as sorbitol, xylitol or mannitol can also be used to replace glucose.[4] Here we tested sorbitol guided wetting in PDMS microwells. The wells have a diameter of 50 µm and a height of 55 µm. The PDMS microwell array was oxidized with air plasma for 2 min, primed with a 40 vol% sorbitol solution

and dried in air (Fig. S5). After storage at room temperature for 7 days, water was added to the PDMS microwell array to assess rewetting guided by sorbitol. Water quickly (25 s) and completely dissolved the sorbitol and no air bubbles were trapped in the microwells (Fig. S5). This result demonstrates that sorbitol functions as effectively as glucose in guiding rewetting in microwells. An additional advantage of sorbitol over glucose is its high solubility in water. The solubility of sorbitol in water is 220 g / 100 mL water (equivalent to 59.6 vol%, which is much higher than that of glucose (91 g / 100 mL water, equivalent to 37.1 vol%). Sorbitol's higher solubility is useful in filling deep microcavities or to guide wetting in dead ends in microfluidic devices.

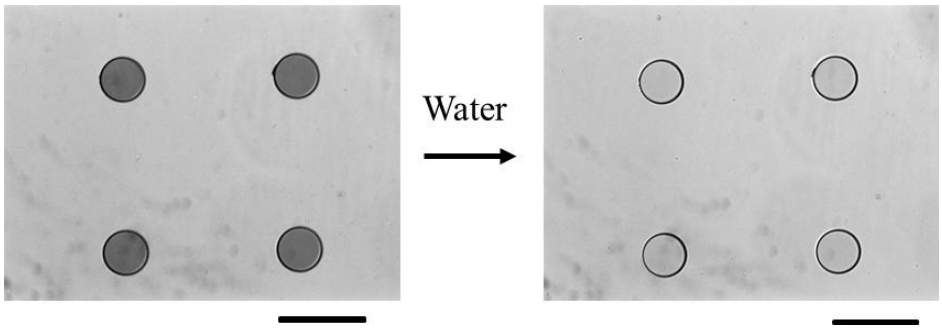


Figure S5. *Transmitted light images showing sorbitol guided wetting in PDMS microwells. Scale bar = 100 μm.*

7. Protocol for priming corners and dead ends of microfluidic channels with glucose or sorbitol

To demonstrate dissolution guided wetting in the corners and dead ends of microfluidic channels, microfluidic chips were constructed by molding PDMS channels from a master and then bonding the PDMS with a glass slide after plasma oxidation of the PDMS (Fig. S6-a). Immediately after plasma treatment and bonding, 5 μL of a monosaccharide solution (in some experiments, the monosaccharide was mixed with 200 μg/mL TRITC dextran) was added to one reservoir of the microfluidic channel (Fig. S6-b). Due to the hydrophilic surface of the freshly plasma-bonded PDMS, the solution spontaneously wet the entire channel within a few minutes, even in corners and dead ends without trapping air bubbles. A hose supplied with nitrogen was placed at the opposite reservoir and used to purge the main microfluidic channel (Fig. S6-c). The solution flushed out at the reservoir was removed by aspiration. A drop of water was added to the reservoir of the main channel during purging to dilute the monosaccharide solution as it exited the channel. The fluid in the reservoir was quickly aspirated after purging. (*Note: this step is essential. The purpose is to completely remove any residual glucose/sorbitol solution at the channel entrance; otherwise, the purged solution would flow back into the main channel and block the channel once solidified.*) After purging, residual solution remained trapped in the dead ends (Fig. S6-d). The chips were then stored at room temperature and the residual monosaccharide solution in the device was allowed to gradually dry by evaporation (Fig. S6-e). In these experiments, a 30 vol% glucose solution was used to fill the corners in a microfluidic channel, and a 50 vol% sorbitol was used to fill the dead ends in a microfluidic channel.

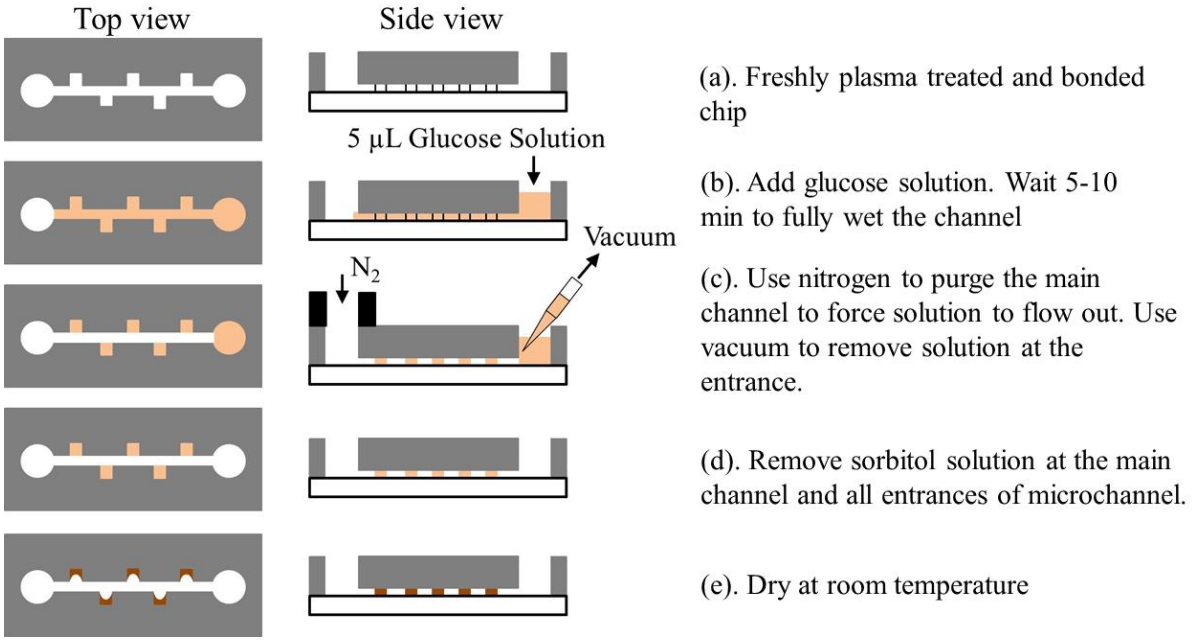


Figure S6. *Process of priming the corners and dead ends of microfluidic channels with a 30 vol% glucose solution or a 50 vol% sorbitol solution.*

8. Videos showing monosaccharide-guided wetting in microwells, corners and dead ends of PDMS microdevices

Video #1 shows the guided wetting by glucose in PDMS microwells (diameter = 100 µm, depth = 55 µm). A 37 vol% glucose solution was used to prime the microwells. The microwell array was stored for 2 months. Water was added to the array at t = 5 s of the video. The glucose was quickly dissolved and the microwells were completely wetted by water (without air bubbles trapped inside the microwells).

Video #2 shows the air bubble trapped in PDMS microwells (diameter = 80 µm, depth = 55 µm). The microwell array was stored for 2 months. Water was added to the array at t = 2 s of the video. Air bubbles were trapped inside the microwells.

Video #3 shows the guided wetting by glucose in corners in a PDMS microfluidic chip. The width of main channel = 50 µm, and the size of square chamber is 500 µm × 500 µm. A 30 vol% glucose solution was used to prime the chip. The chip was stored for 7 days. Water was added to the chip at t = 2 s of the video. The glucose was gradually dissolved and the square chamber was completely wetted by water (without air bubbles trapped in the corners). Complete dissolution of the glucose coating required ~30s.

Video #4 shows air bubble trapped in corners in a PDMS microfluidic chip. The width of main channel = 50 µm, and the size of square chamber is 500 µm × 500 µm. The chip was stored for 7 days. Water was added to the chip at t = 1 s of the video. Air bubbles were trapped in corners.

Video #5 shows the guided wetting by glucose in dead ends in a PDMS microfluidic chip. The width of main channel = 50 μm, and the size of dead ends was 50 μm × 50 μm. A 50 vol% sorbitol solution was used to prime the chip. The chip was stored for 7 days. Water was added to the chip at t = 2 s of the video. The sorbitol was gradually dissolved and the dead ends were completely wetted by water (without air bubbles trapped in the dead ends). Complete dissolution of the sorbitol coating required ~10s.

Video #6 shows air bubble trapped in dead ends in a PDMS microfluidic chip. The width of main channel = 50 μm, and the size of dead ends was 50 μm × 50 μm. The chip was stored for 7 days. Water was added to the chip at t = 1 s of the video. Air bubbles were trapped in dead ends.

References

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4. K. P. Isotupa, S. Gunn, C. Y. Chen, D. Lopatin and K. K. Makinen, *Am. J. Orthod. Dentofac. Orthop.*, 1995, **107**, 497-504.