Supporting Information

Time-Dependent Wetting Behavior of PDMS Surfaces with Bioinspired, Hierarchical Structures

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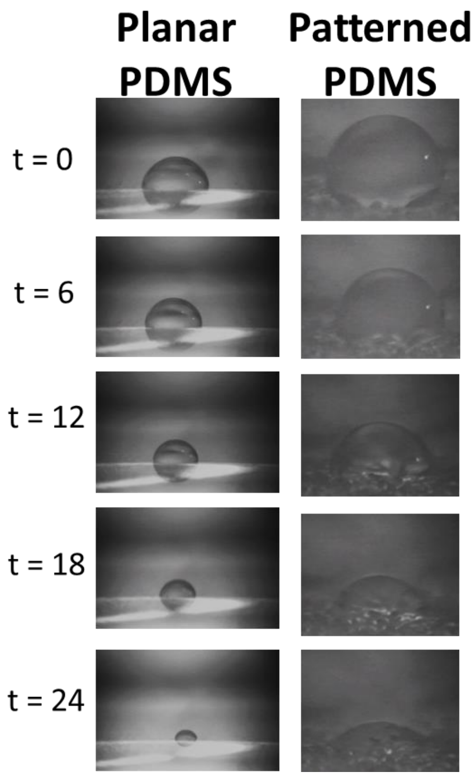

Figure S1. Evaporation of sessile drops of a 40% (by volume) binary mixture of ethanol in water on planar versus sand-dollar-templated PDMS. (a) On planar PDMS, liquid evaporates, decreasing the area of contact, while maintaining a constant contact angle and (b) on sand-dollar-templated PDMS, liquid evaporates, maintaining a constant area of contact, while decreasing the contact angle (Time, *t*, in minutes).

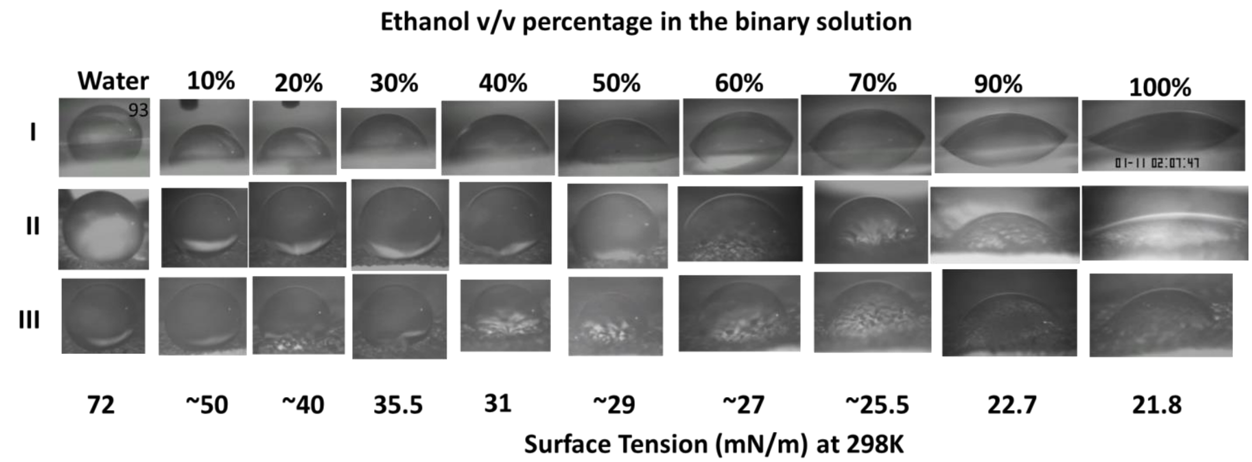

Figure S2. Static contact angles on planar PDMS and sand-dollar-templated PDMS

I: Planar PDMS; II: sand-dollar-templated PDMS; III: FDTS-coated sand-dollar-templated PDMS

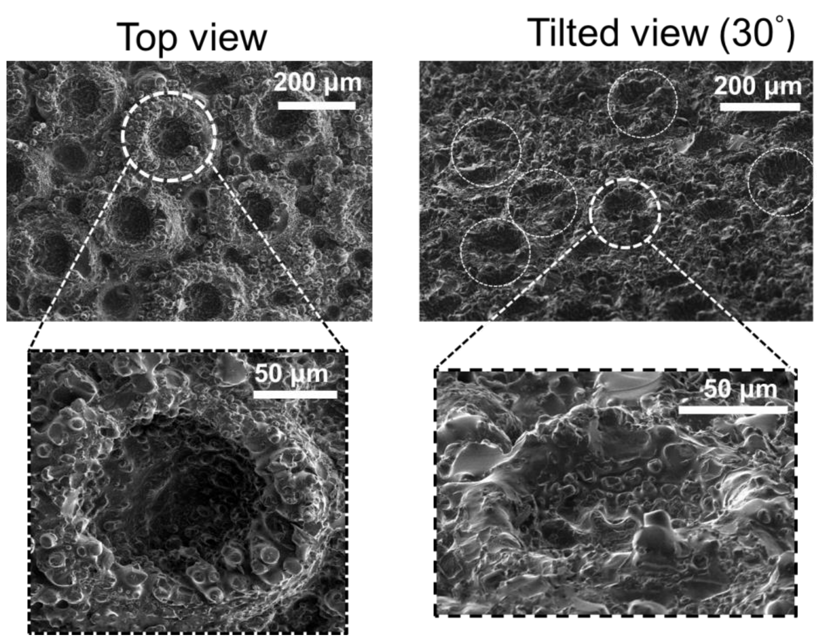

Figure S3. Scanning electron micrographs of a sand-dollar-templated PDMS surface, shown from the (left) top view, and (right) tilted view.

Section S1.

A simple model of the features of sand-dollar-templated (SDT) PDMS surfaces was developed by confocal microscopy and by imaging samples at various tilted angles in a scanning electron microscope (Figures 3 and S3). SDT-PDMS surfaces were covered with cylindrical-shaped features in a roughly hexagonal arrangement. In the model, we arranged hexagonal lattices of rings (Figure 3). As shown schematically below, each cell unit can be in either a partially wetting state, wherein the liquid remains at the top of the features (Cassie), satisfying the intrinsic contact angle, θ_o, and creating a flat liquid-vapor interface, or in a fully wetting (Wenzel) state, wherein the liquid fills the feature, a thermodynamically favorable state, creating a small contact angle.

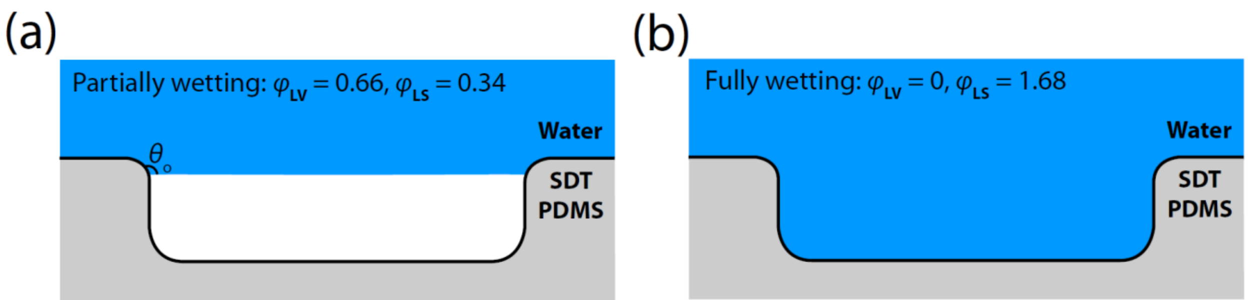

Figure S4. Different wetting states of the ring-shaped features on the surface of sand-dollar-templated PDMS. (a) The partially-filled (Cassie), metastable state and the corresponding values of φ_{LV} and φ_{LS}. (b) The fully-filled (Wenzel), thermodynamically favored state and the corresponding values of φ_{LV} and φ_{LS}.

The apparent contact angle was determined by φ_{LV} (liquid-vapor contact area/projected area), φ_{LS} (liquid-solid contact area/projected area), and θ_{o} (intrinsic contact angle), using the equation $\cos(\theta_{\mathrm{SDT}}) = \varphi_{\mathrm{LS}}\cos(\theta_{\mathrm{o}}) - \varphi_{\mathrm{LV}}$. Thus, in the partially wetting state, $\varphi_{\mathrm{LV}} = (3 \times A_1 + A_3)/(3 \times A_1 + 3 \times A_2 + A_3)$, and $\varphi_{\mathrm{LS}} = (3 \times A_2)/(3 \times A_1 + 3 \times A_2 + A_3)$, where $A_1 = \pi r_i^2$, $A_2 = \pi(r_o^2 - r_i^2)$, and $A_3 = (2r_o \ + 20\ \mu m)^2 3\sqrt{3}/2 - 3\pi r_o^2$, and where r_i and r_o are the inner and the outer radii of the cylinders, respectively. Using the actual dimensions given in Fig. 2, $\varphi_{LV} = 0.66$ and $\varphi_{LS} = 0.34$. In the fully wetting state, $\varphi_{LV} = 0$ and $\varphi_{LS} = (3 \times A_1 + A_3 + A_2 + A_4)/(3 \times A_1 + 3 \times A_2 + A_3)$, where $A_4 = (3 \times 2\pi r_i \ + 3 \times 2\pi r_o \ ) \times 20\ \mu m$, which is the area of the vertical walls of the features. Using the actual dimensions given in Fig. S4, $\varphi_{LS} = 1.68$. Thus, to determine the fraction of unit cells that were fully filled, p, we set $\varphi_{LV} = (1-p) \times 0.66$ and $\varphi_{LS} = (1-p) \times 0.34 + p \times 1.68$. When θ_o is known, p can be determined as a function of θ_{SDT}. For water on SDT-PDMS, p = 0 (Cassie) yields θ_{SDT} = 137° and p = 1 (Wenzel) yields θ_{SDT} = 110°, further indicating that the Wenzel state is thermodynamically favorable.

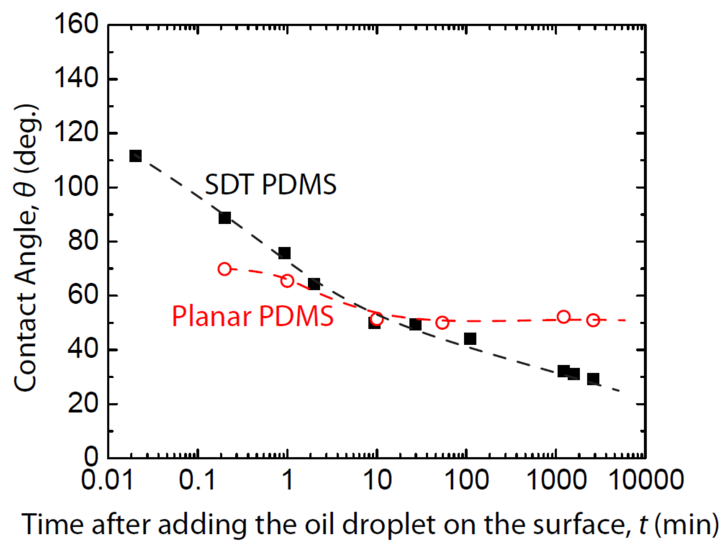

Figure S5. Time-dependent changes in contact angles of sessile canola oil droplets on sand-dollar-templated PDMS versus planar PDMS over 3000 min (50 h).

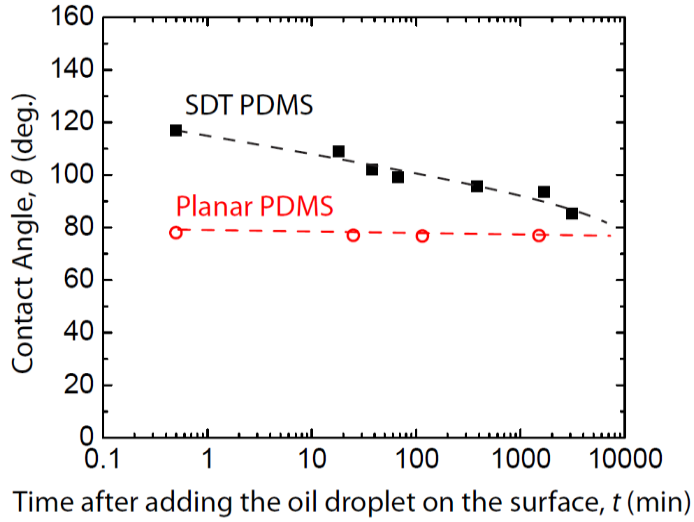

Figure S6. Time-dependent changes in contact angles of sessile canola oil droplets on FDTS-coated sand-dollar-templated PDMS versus planar PDMS over 3000 min (50 h).

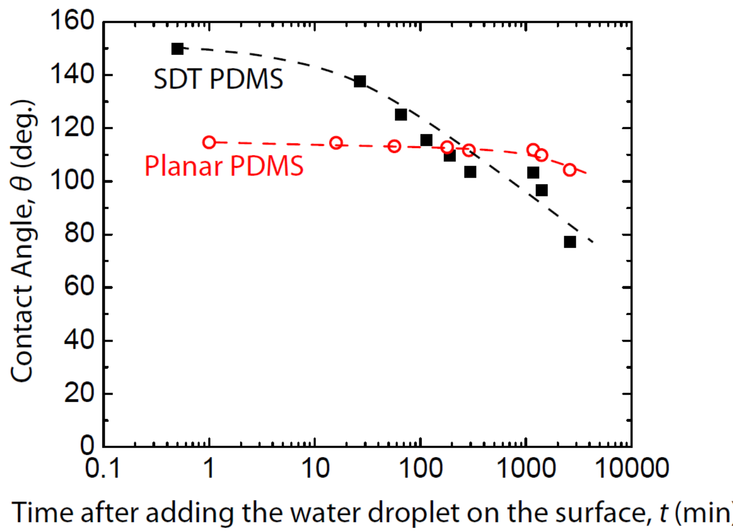

Figure S7. Time-dependent changes in contact angles of sessile water droplets on FDTS-coated sand-dollar-templated PDMS versus planar PDMS over 3000 min (50 h).

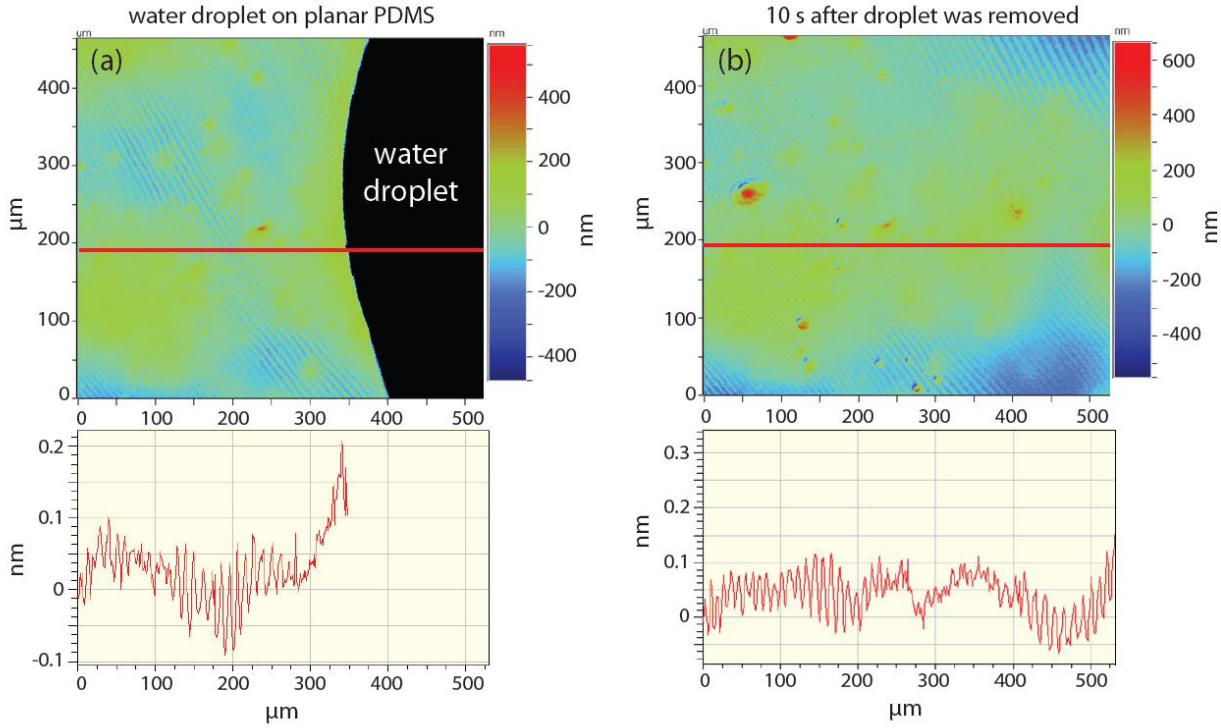

Figure S8. Optical profilometry images of (a) a water droplet sitting on a planar PDMS surface and (b) the PDMS surface 10 s after the droplet was removed. To facilitate imaging the deformations, crosslinked PDMS with a 20:1 ratio (by mass) of polymer to cross-linker was used, as opposed to 10:1 for the contact angle studies. When the droplet sits on the surface, surface deformations near the triple-phase contact line are a minimum of 200 nm high. Note that, because the contact angle is >90°, the droplet occludes the dry PDMS surface nearest to the droplet – an area in which deformations are presumably larger. After the droplet is removed, the surface quickly relaxes. In the more crosslinked PDMS used in the contact angle studies, deformations such as the one shown in (a) should form (and relax) even faster.

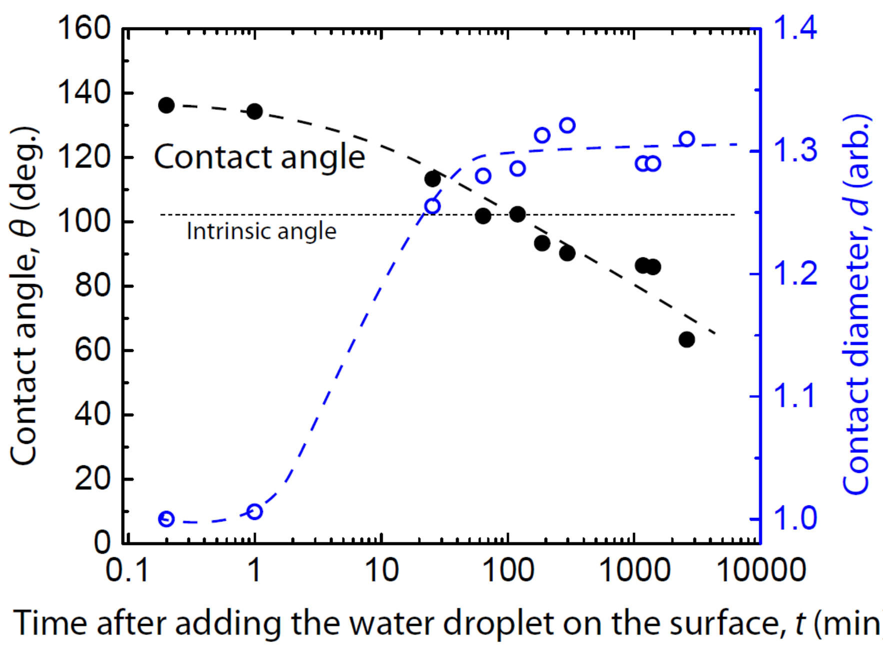

Figure S9. A plot of the contact angle and the diameter of sessile water droplets on sand-dollar-templated PDMS.

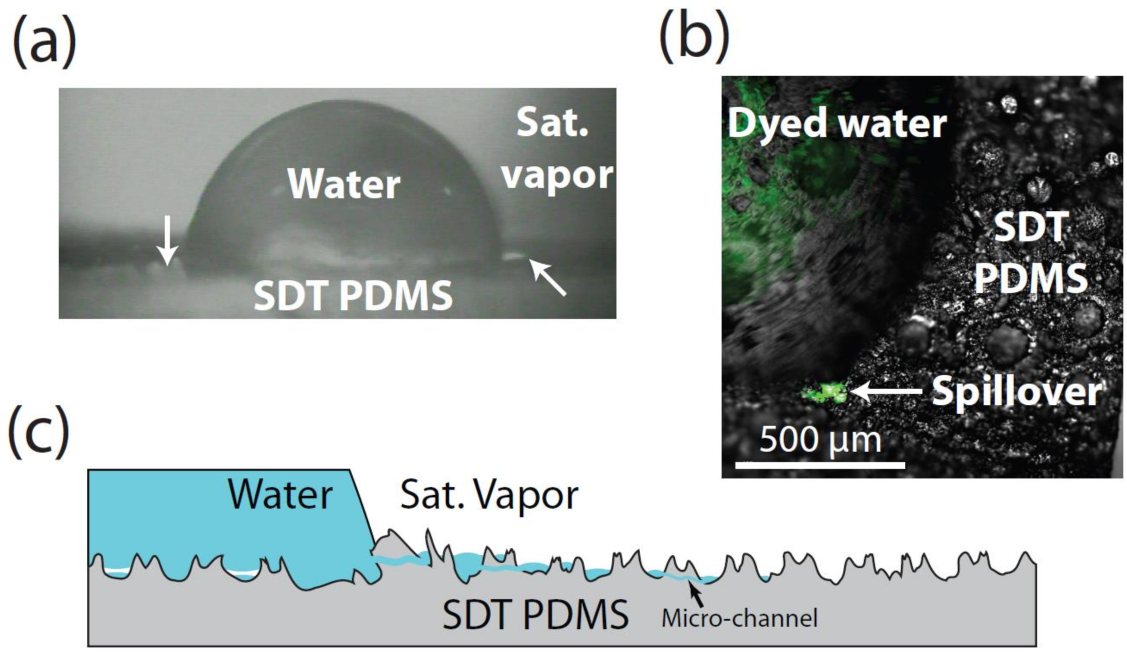

Figure S10. Experimental observations and a schematic of pores filling outside of the contact region during sessile water droplet experiments on sand-dollar-templated PDMS. (a) A water droplet after 4 h on the surface; white arrows indicate where water has pooled. (b) A confocal microscopy image taken 1 h after the fluorescently dyed water droplet was placed on the surface; note the water outside of the contact region. (c) A schematic showing the flow of the droplet outside of the contact region; note the deformation of the triple-phase contact line.

Table S1. Surface tensions of water mixed with different percentage volumes of alcohol.[1]

Percentage volume of ethanol	Surface tension (mN/m)
0.0	72.01
6.3	55.73
12.3	47.53
18.3	42.08
24.1	37.97
29.7	35.51
35.2	32.98
45.8	30.16
55.9	27.96
65.5	26.23
74.7	25.01
83.5	23.82
91.9	22.72
100.0	21.82

Supplemental Experimental Section

FDTS coating of sand dollars. A perfluorotrichlorosilane (FDTS) film was deposited on PDMS via molecular vapor deposition (MVD) (Applied Microstructures Inc.). The process entailed surface activation of PDMS via a UV-ozone plasma treatment at 300 mTorr and 100 W for 5 min followed by MVD: four injections of 0.5 Torr FDTS and then one injection of 6 Torr water with a reaction time of 15 min and 5 purges. Because FDTS is chemisorbed on the PDMS surface, the contact angles were repeatable after multiple weeks.

Profilometry measurements of planar PDMS. Optical profilometry was conducted on an Wyko NT1100 Optical Profiling System. Further details are given in the caption of Figure S8.

References

(1) Vazquez, G.; Alvarez, E.; Navaza, J. M. Surface Tension of Alcohol Water + Water from 20 to 50 °C J. Chem. Eng. Data 1995, 40, 611-614.