Supporting Online Material for

**Designing Superoleophobic Surfaces**

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**This PDF file includes:**

Materials and Methods
SOM Text
Figs. S1 to S10
Tables S1 to S3
Movies S1 to S4
References
MATERIALS AND METHODS

NMR characterization. 29Si NMR data was obtained on a Bruker Axs Smart Apex and chemical shifts were reported in part per million (δ ppm). 29Si NMR was referenced to tetramethylsilane (δ = 0.0) and was measured with inverse-gated proton decoupling with a 12 second pulse delay in order to minimize (negative) nuclear Overhauser effects.

FluoroPOSS synthesis and molecular structure (I):

**Fluorodecyl POSS synthesis.** 1H,1H,2H,2H-Heptadecafluorodecyltriethoxysilane (6.10 g), deionized water (0.27 g), and potassium hydroxide (2.088 mg) were added to a 10 ml volumetric flask. The balance of the volume to 10 ml was filled with ethanol. The contents were transferred to a 25 ml round bottom flask with a Teflon covered magnetic stir bar. The contents were stirred at room temperature overnight under nitrogen. A fine white powder was formed. The product was rinsed with ethanol and dried. A 94.3% yield of pure 1H,1H,2H,2H-heptadecafluorodecyl₈T₈ was obtained. 29Si NMR ((CD₃)₂CO, 59.6 MHz): δ = -67.0.

**Fluoroctyl POSS synthesis.** 1H,1H,2H,2H-Tridecafluorooctyltriethoxysilane (5.10 g), deionized water (0.27 g), and potassium hydroxide (2.088 mg) were added to a 10 ml volumetric flask. The balance of the volume to 10 ml was filled with ethanol. The contents were transferred to a 25 ml round bottom flask with a Teflon covered magnetic stir bar. The contents were stirred at room temperature overnight under nitrogen. A fine white powder was formed. The product was rinsed with ethanol and dried. A 95.1% yield of pure 1H,1H,2H,2H-tridecafluorooctyl₈T₈ was obtained. 29Si NMR ((CD₃)₂CO, 59.6 MHz): δ = -67.0.

**Fluorohexyl POSS synthesis.** Fluorohexyl POSS was prepared by first synthesizing 1H,1H,2H,2H-nonafluorohexyltriethoxysilane, as it was not commercially available. 1H,1H,2H,2H-Perfluorohexene (0.25 mol), trichlorosilane (0.30 mol), and H₂PtCl₆ (0.025 mol, 2 M in isopropanol) were charged in a sealed tube. The vessel was purged with nitrogen, sealed, and placed in a preheated oil bath at 80°C for 24 h. The crude mixture
was fractionally distilled to obtain the 1H,1H,2H,2H-nonafluorohexyltrichlorosilane as a colorless liquid (80%). The pure product is then placed into nine equivalents of neat triethylorthoformate and heated to 110°C for 48 h. The mixture was fractionally distilled to obtain the 1H,1H,2H,2H-nonafluorohexyltriethoxysilane as a colorless liquid (70%). Next, the 1H,1H,2H,2H-Nonafluorohexyltriethoxysilane (4.10 g), deionized water (0.27 g), and potassium hydroxide (2.088 mg) were added to a 10 ml volumetric flask. The balance of the volume to 10 ml was filled with ethanol. The contents were transferred to a 25 ml round bottom flask with a Teflon covered magnetic stir bar. The contents were stirred at room temperature overnight under nitrogen. A fine white powder was formed. The product was rinsed with ethanol and dried. A 91.5% yield of pure 1H,1H,2H,2H-nonafluorohexyl8T8 was obtained. 29Si NMR ((CD3)2CO, 59.6 MHz): δ = -66.9.

**Polymers used.** PMMA (Mw = 540 kDa, PDI ≈ 2.2) was purchased from Scientific Polymer Products, Inc. (catalog no. 037D).

**Spincoating.** Both the polymer and fluoroPOSS were dissolved in a common solvent, Asahiklin AK-225 (Asahi glass co.), at a concentration of 5 mg/ml, and the rotation speed during spincoating was set at 900 rpm.

**Contact angle measurements.** The contact angles for various liquids were measured using a contact angle goniometer, VCA2000 (AST Inc.). The advancing contact angle was measured by advancing a small volume of the probing liquid (typically 2-4 μl) on to the surface, using a syringe. The receding contact angle was measured by slowly removing the probing liquid from a drop already on the surface. For each sample a minimum of four different readings were recorded. Typical error in measurements was ~ 2°.

**Electrospinning.** Both the polymer and fluoroPOSS were dissolved in Asahiklin AK-225 at a concentration of ~ 5 wt%. The solution was then electrospun using a custom-built apparatus as described previously (2) with the flow rate, plate-to-plate distance and voltage set to 0.05 ml/min, 25 cm and 20 kV, respectively.
Scanning electron microscopy. A JEOL-6060SEM (JEOL Ltd., Japan) scanning electron microscope (SEM) was used for imaging. Before imaging, the electrospun surfaces were sputter-coated with a 5-10 nm layer of gold by use of a Desk II cold sputter/etch unit (Denton Vacuum LLC). The micro-hoodoo samples did not need a gold coating, and were tilted to ~30° for imaging.

Micro-hoodoo fabrication. 4” test grade p-type silicon wafers were bought from Wafernet, Inc. A 300 nm thick silicon dioxide thin film was first deposited on a piranha (1:3 mixture of H2SO4 and H2O2) cleaned silicon wafer, by PECVD (plasma enhanced chemical vapor deposition). Cap geometries were defined via standard photolithography using OCG825 as the photoresist. Cap patterns were then transferred onto silicon dioxide using a CF4 plasma reactive ion etching (RIE) process. Etch depth was set to 400 nm to expose bare silicon surface. The caps were then released with severe re-entrance using vapor-phase XeF2 isotropic etching. Finally, the surface was cleaned with piranha. A number of different hoodoo surfaces with spacing (2D) varying between 10 μm – 100 μm were fabricated, in order to vary the fractional surface coverage φs. The feature height and cap width (2W) were held fixed at 7 and 20 μm respectively, while the cap thickness (2R) was kept at ~ 300 nm.

Micro-hoodoo Silanization. The silane treatment was carried out by a chemical vapor deposition of 1H,1H,2H,2H-perfluorodecyltrichlorosilane. Samples were placed in an oven together with the silane and heated at 140°C for 30 minutes.

X-ray photoelectron spectroscopy (XPS). XPS measurements on the electrospun fibers were conducted using a Kratos Axis Ultra X-ray photoelectron spectrometer manufactured by Kratos Analytical of Manchester, England. The monochromatized Al-Kα X-ray source was operated at 15 kV and 10 mA (150W). Photoelectrons were collected at a takeoff angle of 90° relative to the sample surface. Widescan survey spectra were acquired using analyzer pass energy of 160 eV and a step size of 1 eV. Atomic and mass percentages were calculated from the areas of
representative elemental peaks using the library of relative sensitivity factors provided by the manufacturer.
SUPPORTING TEXT.

Section S1. Calculations of pressure required to transition from the metastable Cassie state to the Wenzel state (breakthrough pressure) on electrospun fiber mats.

Figure S1. A and B. SEM micrographs of an electrospun fiber mat. C. A model representation of the electrospun fiber mat surface. D. A schematic illustrating the expected solid-liquid-air interface on the fiber surface in the Cassie state. E. The sagging of the liquid-air interface on the application of external pressure. The sagging interface can impinge upon the next layer of fibers, leading to a Wenzel state.

The electrospun fiber mat is extremely porous with a random distribution of both fibers and cavities within its structure (see Figs. S1A and S1B). To calculate the pressure required for any liquid to breakthrough the fiber mesh, we approximate the electrospun surface by the model surface shown in Fig. S1C.

On the application of external pressure $P$ (in the form of a column of liquid), the liquid-air interface gets distorted, with a curvature $\kappa \approx \frac{P}{\gamma_{lv}}$. This results in sagging
\( h_1 = \frac{1}{k} \left( 1 - \cos \left( \sin^{-1}(D\kappa) \right) \right) \) and a shift in local contact angle, \( \delta \theta = \sin^{-1}(D\kappa) \), where \( 2D \) is the edge to edge distance between the fibers (see Figs. S1D and S1E). If we define the radius of fibers as \( R \), the separation between the liquid contact line and the bottom fiber B is, \( h_2 = R \left( 1 - \cos \theta' \right) (\theta' = \theta - \delta \theta; \) here \( \theta \) is the equilibrium contact angle, and \( \delta \theta \) is the shift in the local contact angle of the liquid due to sagging).

The transition from the metastable Cassie state to the Wenzel state occurs due to the impingement of the sagging liquid-air interface on the next layer of fibers (see Fig. S1E). Thus, the breakthrough pressure can be evaluated as the pressure at which the sagging \( h_1 \) becomes equal to \( h_2 \).
Section S2. Calculations for the change in the Gibbs free energy on the wetting of rough surfaces.

Figure S2. A schematic illustrating the various parameters used in the calculation of the change in the Gibbs free energy density on the propagation of the liquid-air interface, as described below.

As a liquid wets the structure of a solid substrate, the original liquid-air and solid-air interfaces are progressively replaced by the liquid-solid interface, leading to a gain or loss in the overall energy of the system. Marmur (3) used this idea to predict the stability of a composite (Cassie) interface (eq. 9 of reference (3)). We expand Marmur’s work and calculate the actual change in the Gibbs free energy density from a reference point ($\delta G^* = (\text{change in the surface energy of the system}) / (\text{original surface area of drop})$) of a liquid drop associated with the propagation of the solid-liquid interface on a rough substrate.

First, for any given value of the normalized distance of the liquid – air interface from the base of the surface ($h$; normalized with respect to the maximum height of the surface), we assume a number of different values for the temporary apparent contact angle $\theta^*_t$ such that $0^\circ < \theta^*_t < 180^\circ$. Next, we calculate the Gibbs free energy density ($G^*$) of the liquid drop for a given $\theta^*_t$ and $h$, with respect to a reference state of $G^* = 0$ at $h = 1$, as:

$$G^* = \gamma_l \pi R^2 (-2 - 2 \cos \theta^*_t - \sin^2 \theta^*_t (R_\phi \phi_s \cos \theta^*_t + \phi_s - 1)) / 4 \pi R_0^2$$

and $R = R_0 \left( \frac{4}{\sqrt{2 - 3 \cos \theta^*_t + \cos^3 \theta^*_t}} \right)^{1/3}$

where $R = \text{radius of drop in contact with surface}$, $R_0 = \text{original radius of drop (at } h = 1)$, $R_\phi$ is the ratio of the total wet area to the projected wet area and $\phi_s$ is the ratio of the projected wet area: $\phi_s = \frac{A_{\text{wet}}}{A_{\text{projected}}}$.
projected wet area to the total projected area, as shown in Fig. S2. It should be noted that both $R_\phi$ and $\phi_s$ are functions of $h$. Also, the $\theta^*_c$ value which minimizes the Gibbs free energy density will be equal to the apparent contact angle $\theta^*$ computed using the Cassie equation (4) (the Cassie equation collapses to the Wenzel equation when the liquid fully wets the substrate).

To numerically compute $\delta G^*$, we developed a Matlab® (Mathworks Inc.) code with the following steps:

1. Given the data for a surface profile ($z = z(x,y)$), for any value of $h$, find the wetted region by comparing $z$ and $h$ and thus compute $\phi_s$.
2. Integrate to find the total wetted area, and hence compute $R_\phi$.
3. Calculate $\delta G^*$ as a function of $\theta^*_c$, $\phi_s$ and $R_\phi$. A minimum in $\delta G^*$ corresponds to a point of local equilibrium. We also compute the energy barrier around each equilibrium point.

As an introductory example, we calculated the Gibbs free energy density variation for water propagating on a hydrophobic surface ($\theta = 120^\circ$) covered with sinusoidal wrinkles (Fig. S3).

Figure S3. A schematic of a sinusoidal wrinkle on a surface.
The obtained results for this surface are shown in Fig. S4 below:

Figure S4. The change in the Gibbs free energy density, as a function of $\theta^*$ and $h$, for water propagating on a hydrophobic surface with sinusoidal wrinkles on its surface. Here $G^*_{\text{min}}$ is the Gibbs free energy density for the Cassie state. The two minima in Gibbs energy density at $h \sim 0.81$ and $h \sim 0$ correspond to the Cassie and the Wenzel state respectively. The important results for this surface are tabulated in Table S1.

Table S1. A compilation of the significant results obtained from our calculation of the Gibbs free energy density as a function of $\theta^*$ and $h$, for the propagation of water on a hydrophobic surface with sinusoidal wrinkles.

<table>
<thead>
<tr>
<th>Starting values</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic contact angle</td>
<td>120°</td>
</tr>
<tr>
<td>Surface profile (nondimensional)</td>
<td>$z(x,y) = 0.75sin^2(\pi x)$</td>
</tr>
<tr>
<td>Surface tension of the liquid</td>
<td>72.1 mN/m</td>
</tr>
</tbody>
</table>

It can be seen from Fig. S4 that the Cassie state has a much lower free energy density as compared to the Wenzel state, and is therefore the thermodynamically favored state.
However, it is possible to provide enough activation energy to force the droplet to transition to the Wenzel state. This is the idea used in the experiments of Krupenkin et al. (5) who use electrical current and voltage to provide the activation energy required to reversibly transition between the Cassie and Wenzel states on the same surface with water. Other calculations on our surface covered with sinusoidal wrinkles shows that when $\theta = \theta_c = 100^\circ$, the Wenzel state has a lower free energy density as compared to the Cassie state and becomes the thermodynamically favored state.

Similar calculations were performed for the propagation of octane on the micro-hoodoo surface, with $\phi_s = 0.11$ and $\theta = 60^\circ$. The results from those calculations are illustrated in Fig. S5.

**Figure S5.** The change in Gibbs free energy density as a function of $\theta^*$ and $h$, for octane propagating on our micro-hoodoo surface. Here $G_{\text{min}}^*$ is the Gibbs free energy density for the Wenzel state. The two minima in the Gibbs energy density at $h \sim 0.97$ and $h \sim 0$ correspond to the Cassie and the Wenzel state respectively. The inset on the graph shows a zoomed in view around $h \sim 0.97$ to illustrate the local energy density minimization for the Cassie state.

It is seen that the overall energy of the surface can be minimized substantially if the surface transitions from the Cassie state to the Wenzel state, however, there is a significant energy barrier preventing this transition. The results for this surface are tabulated in Table S2.
Table S2. A compilation of the significant results obtained from our calculation of the Gibbs free energy density as a function of $\theta_t^*$ and $h$, for the propagation of octane on our micro-hoodoo surfaces.

<table>
<thead>
<tr>
<th>Starting values</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic contact angle</td>
<td>60°</td>
</tr>
<tr>
<td></td>
<td>Apparent contact angle in the Cassie state</td>
</tr>
<tr>
<td>Surface profile</td>
<td>Micro-hoodoos with $\phi_s = 0.11$</td>
</tr>
<tr>
<td></td>
<td>Difference in $\delta G^*$ between the Cassie and Wenzel states</td>
</tr>
<tr>
<td>Surface tension of the liquid</td>
<td>21.6mN/m</td>
</tr>
<tr>
<td></td>
<td>Activation energy required to transition from the Cassie to the Wenzel state</td>
</tr>
</tbody>
</table>

All of the above analyses assume that the air-liquid interface remains flat as the liquid wets the substrate. This assumption results in an extremely high energy barrier for the transition from the metastable Cassie to the Wenzel state, with calculations yielding breakthrough heights which are significantly larger than those obtained experimentally. The actual transition to the Wenzel state on the hoodoo surfaces occurs at much lower pressures than predicted above due to the sagging of the liquid-air interface, as explained in section S1.
Section S3. Design parameters for re-entrant surfaces.

Figure S6. A cartoon highlighting the formation of a composite interface on a curved surface (for both fibers and micro-hoodoos). The design parameters $R$, $D$, $H$ and $W$ for both the fiber and hoodoo surface are also shown. The blue surface is wetted while the red surface remains non-wetted when in contact with a liquid whose equilibrium contact angle is $\theta$.

The two most important characteristics that need to be considered while designing an extremely hydrophobic or oleophobic surface in the Cassie state are the apparent contact angle ($\hat{\theta}$) and the robustness of the Cassie state.

The apparent contact angle in the Cassie state is determined by $\phi_s$, the fraction of the solid surface wetted by the contacting liquid. For any given equilibrium contact angle $\theta$, the fraction $\phi_s$ on the electrospun fiber surface (see Fig. S6) is controlled by the variable $(R+D)/R (= D^*)$, as originally derived by Cassie and Baxter (4). According to their analysis, $\phi_s = \left(\pi R/(R+D)\right)(1-\theta/180)$. Higher values of $D^*$ lower $\phi_s$ and consequently increase the apparent contact angle $\hat{\theta}$, in accordance with the Cassie equation. However, higher $D^*$ values also lead to more severe sagging of the liquid-air interface (see supporting online text, section S1), which decreases the robustness of the metastable Cassie state and allows for easier liquid penetration through the structure.

The tests by Cassie-Baxter were performed on wire gratings with $1.9 \leq D^* \leq 5.8$. The wire gratings were coated with a paraffin wax having an equilibrium contact angle $\approx 105^\circ$ and as a result they got apparent contact angles between $132.5^\circ - 153^\circ$. On the other hand, for our electrospun fiber mats, $D^* = 9$. This higher value leads to extremely large apparent contact angles ($\approx 145^\circ$) even with liquids having an equilibrium contact angle of $\approx 70^\circ$. The reasons for the robustness of the Cassie state on the electrospun fiber mat surfaces, despite the high $D^*$, are discussed below:

As discussed in supporting online text, section S1, the sagging height of the liquid-air interface ($h_i$) can be calculated to be: 

$$ h_i = 1/\kappa \left(1 - \cos \left(\sin^{-1} \left( D\kappa \right) \right) \right) $$

where $\kappa$ is...
the curvature of the liquid-air interface. Generally, \( \kappa = \frac{\text{pressure}}{2 \gamma \kappa} \) and it becomes the inverse of the capillary length \( l_{\text{cap}} = \sqrt{\frac{\gamma}{\rho g}} \) for liquid droplets on a surface in the absence of any external pressure.

The system transitions from the Cassie to the Wenzel state when the sagging height \((h_1)\) becomes equal to the original clearance between the liquid-vapor interface and the next level of fibers, \( h_2 = R(1 - \cos \theta) \) (neglecting any shift in contact angle due to sagging). When \( D \ll 1/\kappa \) \((1/\kappa \approx l_{\text{cap}})\), \( \sin(D\kappa) \approx D\kappa \). Thus,

\[
\begin{align*}
h_1 &\approx 1/\kappa(1 - \cos(D\kappa)) \\
&= \frac{1}{\kappa} \left(1 - \sqrt{1 - \sin^2(D\kappa)}\right) \\
&\approx \frac{1}{\kappa} \left(1 - \sqrt{1 - (D\kappa)^2}\right) \\
&\approx \frac{1}{\kappa} \left(1 - (1 - (D\kappa)^2)/2\right) = \frac{2}{\kappa(D\kappa)^2}
\end{align*}
\]

Therefore, the ratio,

\[
\frac{h_2}{h_1} \approx \frac{R}{\kappa} \left(1 - \cos \theta\right) \left\{\frac{\left(D\kappa\right)^2}{2}\right\} = 2 \left(1 - \cos \theta\right) \frac{R l_{\text{cap}}}{D^2} = \frac{H^*}{D^2}
\]

We call the variable \( H^* \) the robustness parameter as it correlates the robustness of the metastable Cassie state to the fluid properties, the equilibrium contact angle, as well as the geometry of the substrate.

Varying the radius \((R)\) and spacing \((D)\) of the electrospun fibers has competing effects on the apparent contact angles and the stability of the composite interface. Further, it can be deduced from the definition of the design parameters \( D^* = (R+D)/R \) and \( H^* = 2 \left(1 - \cos \theta\right) \frac{R l_{\text{cap}}}{D^2} \) that \( H^* \) is more sensitive to variations in both \( D \) and \( R \), as compared to \( D^* \). Thus, the metastable Cassie state may not be accessible on every surface that possesses re-entrant curvature, depending on the applied pressure required to transition irreversibly from the metastable Cassie to the Wenzel state. For our electrospun fibers an \( H^* \) value greater than \( \approx 10 \) (using a constant value for both \( R \) and \( D = 500 \text{ nm} \) and \( 4 \mu\text{m} \) respectively) leads to a stable Cassie state for a liquid droplet \( \sim 1\text{mm} \) in diameter. This \( H^* \) value is much larger than 1 because of our approximation of the fiber geometry and our ignoring of the macroscopic vibrational energy of the drop.
Due to the relatively low values of $H^*$, our electrospun fiber mats with low POSS concentrations are easily wetted by octane, and even fibers with higher POSS concentrations are susceptible to octane penetration at moderate applied pressures. Our calculations, shown in supporting online text, section S1, reveal that octane has a breakthrough height of ~ 50 mm on an electrospun surface with 44 wt% POSS, which matches well with our measured values, as shown in Fig. 1D.

Hence, we designed our micro-hoodooos to provide a more robust metastable Cassie state especially with low surface tension liquids. For this re-entrant geometry, $\phi_s = \left(\frac{W}{W + D}\right)^2$. Thus the design parameters have the new form $D^* = \left(\frac{W + D}{W}\right)^2$ and $H^* = 2\left((1 - \cos \theta)R + H\right)_{cap}/D^2$ for this geometry. As the two hoodoo spacing ($W$) and height ($H$) can be varied independently (see Fig. S6), we can easily decouple the two design parameters and attain both high apparent contact angle and high robustness at the same time. Moreover, the effect of the equilibrium contact angle $\theta$ on the robustness is minimized, as $H$ is typically much larger than $R$.

Typical design parameters and characteristics of the original Cassie-Baxter wire grating, our electrospun fiber mats, and the micro-hoodooos are presented in Table S3.

**Table S3.** Values of the design parameters, as well as the characteristics of the original Cassie-Baxter (4) wire grating, the electrospun fiber mats, and the micro-hoodooos.
<table>
<thead>
<tr>
<th></th>
<th>Cassie-Baxter’s wire mesh</th>
<th>Electrospun fiber mats</th>
<th>Micro-hoodoos</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^* = (R+D)/R$ or $((W+D)/W)^2$</td>
<td>1.9 – 5.8</td>
<td>9</td>
<td>2.3 – 9</td>
</tr>
<tr>
<td>Fraction of wetted surface - $\phi_s$</td>
<td>0.23 – 0.68</td>
<td>0.2</td>
<td>0.11 - 0.44</td>
</tr>
<tr>
<td>(Equilibrium) and apparent contact angles - for water(^1) and octane(^2)</td>
<td>$1,(105^\circ)$ and $132.5^\circ - 153^\circ$</td>
<td>$1,(76^\circ - 123^\circ)$ and $130^\circ - 161^\circ$</td>
<td>$1,(10^\circ)$ and $155^\circ$(^{oa})</td>
</tr>
<tr>
<td>$H^* = 2(1-\cos \theta)Rl_{cap}/D^2$ or $2((1-\cos \theta)R+H)l_{cap}/D^2$ - for water</td>
<td>3.42 – 34.2</td>
<td>101 – 207</td>
<td>96 – 1560</td>
</tr>
<tr>
<td>$H^* = 2(1-\cos \theta)Rl_{cap}/D^2$ or $2((1-\cos \theta)R+H)l_{cap}/D^2$ - for octane</td>
<td>0.76 – 7.6(^b)</td>
<td>0.1 – 57</td>
<td>64 – 1040</td>
</tr>
<tr>
<td>Surface properties</td>
<td>Hydrophobic</td>
<td>Superhydrophobic, Oleophobic</td>
<td>Superhydrophobic, Superoleophobic</td>
</tr>
</tbody>
</table>

\(^a\) For $\phi_s = 0.11$

\(^b\) The calculations for $H^*$ have been performed assuming an equilibrium contact angle of $60^\circ$ for octane.
Section S4. Estimation of solid surface energy ($\gamma_{sv}$)

As discussed in the manuscript, to enable the formation of a composite interface (Cassie state) on any surface without re-entrant structure, the equilibrium contact angle $\theta$ must be greater than $90^\circ$. Previous work by Shibuichi et al. has argued that for a chemically homogeneous, smooth surface to exhibit $\theta > 90^\circ$ with any liquid, its surface energy $\gamma_{sv}$ must be less than one-fourth the liquid surface tension, $(\gamma_{lv})/4$ (6, 7). Careful studies of monolayer films by Zisman et al. (8) show that the contributions to the overall magnitude of surface energy of a flat surface decreased in the order -CH$_2$ > -CH$_3$ > -CF$_2$ > -CF$_2$H > -CF$_3$, and based on this analysis, the lowest solid surface energy is estimated to be $\sim 6.7$ mN/m (for a hexagonally closed packed monolayer of –CF$_3$ groups on a surface) (8, 9). Taken in conjunction, these studies explain the absence of non-wetting surfaces displaying equilibrium contact angles $> 90^\circ$ with decane and octane (6-8, 10, 11), as a solid surface would need to have a surface energy of $\sim 5$ mN/m to display $\theta > 90^\circ$ with these liquids.

However, recently a few groups have reported extremely low $\gamma_{sv}$ values; for example Coulson et al. (10, 12) report surface energy values as low as 1.5 mN/m for coatings created by pulsed plasma polymerization of 1H,1H,2H-perfluoro-1-dodecene.

Thus, the issue of the minimum surface energy seems to be a bit controversial and unresolved in the literature. The problem stems from the fact that measurement of equilibrium contact angles only provides an indirect estimate of the surface energy, and typically involves extrapolation or assuming an additive decomposition of $\gamma_{sv}$ into dispersive and H-bonding / polar contributions. The most accurate determination of surface energies requires the measurement of the work of adhesion, and this is not often done (13).

There are several different methods of using contact angles to estimate the surface energy of a material (e.g. the Zisman analysis (8), the Owens-Wendt analysis (14), and Girifalco-Good-Fowkes-Young (15, 16) analysis), and each of these methods typically yields a different value for the computed surface energy, depending on the surface under study. Thus, previous studies have noted that these methods should only be used to obtain an estimate of the actual surface energy, which can be useful in comparing and ranking
different surfaces (say with different degree of fluorination) as long as the same method is used for each surface (13).

Indeed, Coulson et al. also report two different measures of surface energy. They obtain values of $\gamma_{sv} = 1.5\ \text{mN/m}$ (on a smooth glass substrate coated by pulsed plasma polymerization of 1H,1H,2H-perfluoro-1-dodecene (12)) and 4.3 mN/m (on a smooth glass substrate coated by pulsed plasma polymerization of 1H,1H,2H,2H-heptadecafluorodecyl acrylate (10)) using the Zisman analysis, or $\gamma_{sv} = 8.3\ \text{mN/m}$ (12) and 10 mN/m (10) using the Owens-Wendt method for the same two surfaces. It is therefore unclear as to which method provides a more accurate value for $\gamma_{sv}$. An indication that the Zisman analysis might be providing a $\gamma_{sv}$ value lower than the actual value for their surface comes from the values of octane contact angles obtained by Coulson et al. As mentioned above, if $\gamma_{sv} < \gamma_v/4$, the equilibrium contact angle $\theta$ measured experimentally should be greater than 90°. In contrast, Coulson et al. report values of $\theta_{adv} = 74^\circ$ and $\theta_{rec} = 35^\circ$ respectively on their coatings of 1H,1H,2H-perfluoro-1-dodecene when using octane ($\gamma_v = 21.7\ \text{mN/m}$).

We have also computed the surface energy of our spincoated PMMA + fluoroPOSS surfaces using the Zisman and the Owens-Wendt methods. For a spincoated surface containing 44.4 wt% POSS we obtain values of $\gamma_{sv} = -3\ \text{mN/m}$ and $\gamma_{sv} = 7.8\ \text{mN/m}$ (with the dispersive component of surface energy, $\gamma_d = 6.6\ \text{mN/m}$ and the polar component, $\gamma_p = 1.2\ \text{mN/m}$) using the Zisman and the Owens-Wendt method respectively. Fig. S7 shows the Zisman analysis for four different spincoated PMMA + fluoroPOSS films, as well as, the data for the Zisman analysis done by Coulson et al. (10).

Clearly, the negative value of the surface energy obtained from the Zisman analysis of our surfaces are spurious (and arise solely form the extrapolation process employed), however, these calculations again point out the limitations of the various methods that use measurements of equilibrium contact angles to compute $\gamma_{sv}$. It is however clear from the data in Fig. S7 that, as would be expected, the surface energy of our PMMA + fluoroPOSS blends decreases with increasing POSS concentration and for high fluoroPOSS concentrations, the calculated interfacial energy seems to approach
values consistent with those obtained by Coulson et al.

Figure S7. Zisman plot for various spincoated PMMA+fluoroPOSS films. The data from the Zisman analysis performed by Coulson et al. (10) for surfaces prepared by pulsed plasma polymerization of 1H,1H,2H,2H-heptadecafluorodecyl acrylate are also included for comparison.
SUPPORTING FIGURES.

Figure S8. Conferring oleophobicity to a lotus leaf. A. A drop of water (colored with methylene blue) on a lotus leaf surface. The inset shows an SEM micrograph of the lotus leaf surface; the scale bar is 5 μm. B. The wetted surface of the lotus leaf after contact with a droplet of hexadecane. C and D. Droplets of water and hexadecane (colored with ‘oil red O’) on a lotus leaf surface covered with electrospun fibers of PMMA + 44 wt% fluorodecyl POSS. A reflective surface is visible underneath the droplets in both pictures, indicating the presence of microscopic pockets of air.
Figure S9. XPS analysis of electrospun fibers. This figure shows the mass concentration of fluorine on the surface of the electrospun PMMA + fluoroPOSS fibers as a function of the expected mass concentration of fluoroPOSS in the bulk phase of the fiber, if there was no surface migration. This data was obtained through X-ray photoelectron spectroscopy (XPS). It is clear that the low surface energy of the fluoroPOSS molecules enables them to migrate to the fiber surface during the electrospinning process.
Figure S10. A generalized non-wetting diagram comparing the contact angles for various alkanes on the electrospun and spincoated surfaces. The re-entrant fiber surfaces allow for the formation of a composite interface (Cassie state) even with $\theta < 90^\circ$. The surfaces in the lower right quadrant of this diagram correspond to oleophilic substrates that are rendered oleophobic, purely by topography.
SUPPORTING REFERENCES:


**Movie S1.** This video highlights the formation of a reflective surface when a glass slide coated with a superhydrophobic electrospun surface (fibers containing 44 wt% fluorodecyl POSS) is submerged under water. The superhydrophobic surface is inserted in water multiple times and in each case it forms a mirror surface and comes out of water completely dry. (Quicktime; 2.6MB)

**Movie S2.** This video demonstrates the utility of our electrospun fiber mats (fibers containing 9.1 wt% fluorodecyl POSS) as oil – water separating membranes. Octane droplets (red) easily pass through the membrane whereas water droplets (blue) bead up on the surface. (Quicktime; 2.8MB)

**Movie S3.** This video shows a water droplet advancing on untreated SiO2 micro-hoodoos (2D = 10 μm, D* = 2.3, H* = 1560 for water). Although the micro-hoodoos are fabricated from extremely hydrophilic SiO2 (θ ≈ 10°), the water droplet does not penetrate into the hoodoo textured surface. Air pockets between the micro-hoodoos and the water droplet are clearly visible, which is an obvious signature of the Cassie state. (Quicktime; 184kB)

**Movie S4.** This video shows a water droplet receding from the untreated SiO2 micro-hoodoos (2D = 10 μm, D* = 2.3, H* = 1560 for water). The video highlights the high hysteresis (Δθ* ≈ 39°) on the textured surface; however, it is clear that the water droplet has not reached the SiO2 surface at the base of the hoodoos, in which case it would have been impossible to withdraw the water droplet completely. (Quicktime; 260kB)