Fabrics with Tunable Oleophobicity

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Extreme wetting behavior, namely super-repellency and superwetting has recently generated immense commercial and academic interest^[1–10] due to its wide applicability in various fields, including the development of self-cleaning surfaces,^[11] liquid-liquid separation membranes,^[12] and anti-fogging films.^[13] Various research groups have also tried to develop surfaces that can effectively switch their surface wetting properties in response to changes in their surrounding environment.^[14] This includes surfaces that alter their wettability in response to changes in temperature,^[8] electrical voltage,^[15,16] and mechanical deformation.^[17,18] Because of the difficulty in producing surfaces that are strongly repellent to low-surface-tension liquids, such as oils and alcohols, most work on switchable wettability has focused on studies with water droplets^[10] (with the exception of recent work of Ahuja et al.^[15]). In our previous work, we demonstrated how the incorporation of re-entrant surface texture (that is, a multivalued surface topography) in conjunction with surface chemistry can be used to fabricate superoleophobic surfaces, that is, surfaces that can support a robust composite (solid-liquid-air) interface and display contact angles greater than 150° with various low-surface-tension liquids.^[19] More recently, we also developed two general design parameters that can aid the systematic design of omniphobic surfaces that resist wetting by almost any liquid.^[20]

In the present work, we analyze the consequences of these nonwetting design parameters more extensively. Recognizing the role of re-entrant surface features, we first develop a simple dip-coating process for delivering a conformal coating of fluorodecyl polyhedral oligomeric silsesquioxane (POSS) molecules.^[19,21] This coating enables us to bestow substantially enhanced liquid repellency to any substrate possessing re-entrant textures, such as the lotus leaf, commercial fabrics, and even duck feathers, by promoting the formation of a composite (solid–liquid–air) interface. Consideration of the geometric scaling of the design parameters suggests that mechanically deforming a

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re-entrant structure such as a dip-coated commercial fabric will lead to a dramatic, but reversible, reduction in the liquid repellency of the surface. Indeed, we observe that a non-wetting drop (initially sitting on the surface in a composite Cassie–Baxter state) completely wets into the fabric texture beyond a critical imposed strain, leading to near-zero contact angles. This allows us to develop, for the first time, surfaces that exhibit reversible, deformation-dependent, tunable wettability, including the capacity to switch their surface wetting properties (between superrepellent and super-wetting) against a wide range of polar and nonpolar liquids.

When a liquid contacts a textured surface, such as the one shown in Figure 1a, then, provided the pressure difference across the liquid–air interface is negligible, the liquid does not completely penetrate into the pores of the surface texture. Instead, the liquid wets the pore surface partially, until the local angle (ψ) between the liquid and the textured substrate becomes equal to the equilibrium contact angle θ (given by Young's relation^[22]) for the three-phase contact line.^[23–25] The existence of points on the surface that enable the condition $\psi = \theta^{[26]}$ to be fulfilled is a necessary, though not sufficient, condition^[19,24,25,27,28] for the formation of a composite interface, such as the one shown in Figure 1a.

The apparent contact angle θ^* for the composite interface that exists under a strongly nonwetting droplet is typically computed using the Cassie–Baxter relation:

$$\cos\theta^* = f_1 \cos\theta + f_2 \cos\pi = f_1 \cos\theta - f_2 \tag{1}$$

where f_1 is the ratio of the total area of solid–liquid interface to a unit projected area of the textured substrate and f_2 is the corresponding ratio for the liquid–air interface.^[23] An example of a natural surface that is able to support a composite interface is shown in Figure 1b, illustrating water ($\gamma_{1v} = 72.1 \text{ ms m}^{-1}$) droplets "beading up" on the surface of a duck feather. The feather is composed of a periodic array of micrometer-scale cylindrical barbules (see scanning electron microscopy (SEM) images in Supporting Information). The bright, reflective surface visible underneath the water droplet in Figure 1b is a signature of trapped air and the establishment of a composite solid–liquid–air interface. The formation of this "Cassie–Baxter" state enhances super-repellency by promoting a high apparent contact angle (θ^*) and low contact angle hysteresis (defined as the difference between the advancing and receding contact angles) when $f_1 < < 1$.^[23,29–32]

On the other hand, if the liquid fully penetrates into the texture surface, then the apparent contact angle $\boldsymbol{\theta}^*$ is determined by the Wenzel relation:^[33]

 $\cos\theta^* = r\cos\theta$



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Figure 1. a) Schematic diagram illustrating the expected liquid-air interface on a textured surface with an equilibrium contact angle $\theta \sim 100^{\circ}$. In this schematic, the sagging of the liquid-air interface caused by any pressure differential across the interface is ignored. b) Droplets of water (colored with methylene blue) on a duck feather. c) Schematic illustrating the putative liquid-air interface on a textured surface with an equilibrium contact angle $\theta \sim 70^{\circ}$. The sagging angle ($\delta\theta$) is the difference between the equilibrium contact angle (θ) and the local texture angle (ψ). d) Droplets of hexadecane ($\gamma_{1v} = 27.5 \text{ ms m}^{-1}$, colored with Oil Red O) on a dip-coated duck feather. A reflective surface is visible under the droplets in the image, indicating the presence of microscopic pockets of air due to the formation of a composite interface.

where *r* is the surface roughness, defined as the ratio between the actual surface area and the projected area. Since *r* is necessarily greater than unity, roughness amplifies both the wetting and nonwetting behavior of materials in the Wenzel regime, that is, $\cos\theta^* >> 0$ if $\cos\theta > 0$ and $\cos\theta^* << 0$ if $\cos\theta < 0$. A consequence of this dependence on the roughness of the texture is that, once initiated, the imbibition of a liquid drop into a roughened texture can rapidly lead to superwetting, because the apparent contact angle $\theta^* \rightarrow 0^\circ$ when r >> 1 and $\theta < 90^\circ$.

Development of extremely liquid-repellent surfaces requires the design of substrates that promote the formation of a composite interface with any liquid. The two important characteristics of a composite Cassie-Baxter state on a textured surface with a particular contacting liquid are i) the magnitude of the apparent contact angle θ^* on the composite interface and ii) the robustness of the composite interface against external perturbation. The equilibrium apparent contact angles on a textured surface can be readily estimated using the Cassie-Baxter relation (Eq. 1), and in our recent work we developed a dimensionless design parameter A^* to predict the robustness of the composite interface.^[20] This robustness factor represents the ratio between the breakthrough pressure required to cause sufficient sagging and disruption of the liquid-vapor interface (see Fig. 1c) and a characteristic reference pressure P_{ref} , given as $P_{\rm ref} = 2\gamma_{\rm lv}/l_{\rm cap}$, where $l_{\rm cap} = \sqrt{\gamma_{\rm lv}/\rho g}$ (here ho is the fluid density and g is the acceleration due to gravity). This reference pressure $P_{\rm ref}$ is close to the minimum pressure difference across the composite interface for millimetric or larger liquid droplets or puddles,^[20] and the breakthrough pressure at which a given composite interface is disrupted can be computed as $P_{\text{breakthrough}} \approx A^* \times P_{\text{ref}}$.

For a texture that is dominated by periodic cylindrical features, such as the duck feathers shown in Figure 1 and the fabric surface shown in Figure 3, the robustness factor A^* is given as (see Supporting Information):

$$A^* = \frac{P_{\text{breakthrough}}}{P_{\text{ref}}} = \frac{Rl_{cap}}{D^2} \frac{(1 - \cos\theta)}{(1 + 2(R/D)\sin\theta)}$$
(3)

where *R* is the fiber radius and *D* is half the inter-fiber gap, as shown in Figure 1a. Large values of the robustness factor $(A^* >> 1)$ indicate the formation of a robust composite interface with very high breakthrough pressures. On the other hand, as A^* approaches unity, $P_{\text{breakthrough}}$ decreases toward P_{ref} . Thus, a composite interface on any surface for which $A^* < 1$ cannot maintain its stability against even small pressure differentials across the liquid–air interface, causing the liquid to penetrate into the textured surface and ultimately be fully imbibed.

It is also useful to define another dimensionless parameter, D^* , that characterizes the geometry of the re-entrant features. For a texture consisting of uniform cylindrical features as shown in Figure 1a, the ratios f_1 and f_2 in the Cassie–Baxter relationship^[23] (Eq. 1) become $f_1 = R(\pi - \theta)/(R + D)$ and $f_2 = 1 - R \sin \theta/(R + D)$. Substituting these expressions into Equation 1 and factoring out a dimensionless spacing ratio $D^* = (R + D)/R$ enables us to express the apparent contact angle in terms of a purely geometric factor and a contribution involving the equilibrium contact angle on a flat surface:

$$\cos\theta^* = -1 + \frac{1}{D^*} [\sin\theta + (\pi - \theta)\cos\theta]$$
(4)

Higher values of D^* correspond to a higher fraction of air in the composite interface (f_2 in Eq. 1), and consequently an increase in the apparent contact angle θ^* for a given liquid. Care must be taken in developing appropriate expressions for D^* and A^* for surfaces with variable surface texture parameters or multiple scales of roughness, such as commercial fabrics or a lotus leaf (see Supporting Information for further details).^[34,35]

To achieve both high apparent contact angles with low contact-angle hysteresis and a robust composite interface, we seek to maximize the two design parameters D^* and A^* simultaneously. However, for a periodic geometry of cylindrical features, these two design factors are strongly coupled. Increasing the value of D^* by either increasing D or reducing R (with the other geometric variable held constant) leads to a decrease in the values of A^* (see Eq. 3). This coupling is further highlighted in Figure 2, which shows a general design chart for a typical oil (rapeseed oil; $\gamma_{\rm lv} = 35.7 \,\rm m_N \,m^{-1}$, $\theta = 86^\circ$) on a surface with cylindrical fibers, illustrating the variation in the robustness factor A^* with the variation in the spacing ratio D^* . The solid lines in the graph correspond to A^{*} values computed by changing the interfiber distance (D) while maintaining the fiber radius (R) constant. Each solid line corresponds to a different value of the fiber radius R, varying between 1 mm and 1 nm.



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Figure 2. Computed robustness parameter A^* for rapeseed oil $(\gamma_{lv}=35.7 \text{ mN m}^{-1}, \theta=86^{\circ})$ on a surface texture composed of periodic cylindrical features as a function of the spacing ratio $D^* = (S + D)/R$. Values of the robustness parameter for various uncoated (unfilled symbols) and dip-coated surfaces (filled symbols) against rapeseed oil are also shown. A* calculations for the noncoated surfaces are based on the assumption that $\theta = 20^{\circ}$.



Figure 3. a) SEM image of a lotus leaf illustrating its surface texture. The inset shows that droplets of rapeseed oil easily wet the surface of a lotus leaf ($\theta^* \approx 10^\circ$). b) SEM image of a lotus-leaf surface after the dip-coating process. The inset shows that the dip-coated leaf can repel rapeseed oil with an apparent contact angle $\theta^* \approx 145^\circ$. c) SEM image of the polyester fabric. In spite of the presence of the re-entrant curvature, hexadecane can readily wet the fabric surface (inset). d) SEM image of the dip-coated polyester fabric. The inset shows the elemental mapping of fluorine obtained using EDAXS. e) Superrepellency of a dip-coated polyester fabric against various polar and nonpolar liquids.

Evaluating the magnitude of the robustness factor A^* also explains why rapeseed oil spontaneously penetrates the texture of many naturally re-entrant superhydrophobic surfaces such as a duck feather or a lotus leaf (see inset of Fig. 3a, $D^* \approx 58$; also see Supporting Information). In each case, $\overline{A}^* <<1$, as shown in Figure 2. To enable these surfaces to support a composite interface with various low-surface-tension liquids, it is essential to increase the magnitude of the robustness factor A^* . For a fixed surface texture, such an enhancement can be induced most readily by markedly lowering the surface energy of the solid, leading to increased values of the equilibrium contact angle θ (based on the Young's relation^[22]).

In our recent work,^[19,21] we discussed the synthesis and application of a new class of POSS molecules, in the silsesquioxane cage is surrounded which bv 1H,1H,2H,2H-heptadecafluorodecyl groups. These molecules are referred to as fluorodecyl POSS.^[21] The high concentration of perfluorinated carbon atoms in the alkyl chains leads to an extremely low solid-surface energy for these molecules $(\gamma_{sv} \approx 10 \text{ mn m}^{-1}).^{[20]}$ As a comparison, the surface energy of Teflon is $\gamma_{sv} \approx 18 \text{ mn m}^{-1}.^{[36]}$ To provide a conformal and flexible coating of fluorodecyl POSS molecules on any preformed substrate possessing re-entrant texture, we have developed a simple dip-coating procedure using fluorodecyl POSS and a thermoplastic elastomeric binder (see Experimental). After dip-coating, the equilibrium contact angle for rapeseed oil on a smooth glass slide increases to $\theta = 86^{\circ}$; compared to $\theta \approx 0^{\circ}$ on a clean uncoated glass slide (see Supporting Information for contact angle measurements with selected polar and nonpolar liquids on a dip-coated glass slide). Dip-coating also increases the value of the robustness factor for rapeseed oil on a duck feather and a lotus leaf to $A^* \approx$ 4.2 (assuming $R = 1 \ \mu\text{m}$, $D = 20 \ \mu\text{m}$) and $A^* \approx 26$ (assuming $R_{\rm nub} = 2.5 \,\mu$ m, $D_{\rm nub} = 5 \,\mu$ m), respectively (also see Fig. 2). Note that because the lotus leaf does not possess a cylindrical surface texture, the robustness factor A^{*} for the lotus leaf cannot be computed using Equation 3, but requires a more complex expression.^[20] As a result of the high values of the robustness factor, a dip-coated duck feather is able to support a composite interface even with hexadecane ($\gamma_{lv} = 27.5 \text{ m}\text{ m}^{-1}$; $A^* = 3.3$), as shown in Figure 1d.

In Figure 3b we show an SEM image highlighting the surface texture of a dip-coated lotus leaf. A comparison with the surface morphology of an uncoated lotus leaf (Fig. 3a) shows that all of the surface details, even features in the sub-micrometer range, are preserved after dip-coating. The inset in Figure 3b shows that the dip-coating process turns the surface of the leaf oleophobic, allowing it to support a robust composite interface with rapeseed oil and display large apparent contact angles ($\theta^* = 145^\circ$).

Another general class of textured substrates possessing re-entrant curvature is commercial fabrics.^[37–40] Figure 3c shows an electron microscopy image of a commercial polyester fabric (Anticon 100 clean-room wipe). The inset in Figure 3c shows that a droplet of hexadecane completely wets the surface of the as-received polyester fabric. Figure 3d shows the surface morphology of a polyester fabric dip-coated with fluorodecyl POSS. It is clear that all surface details of the polyester fabric are preserved after dip-coating. The inset in Figure 3d shows the elemental mapping of fluorine on the dip-coated fabric surface using energy-dispersive X-ray scattering (EDAXS). Dip-coating



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provides a conformal coating of fluorinated molecules on the fabric surface. The liquid repellency of the dip-coated fabric is highlighted in Figure 3e, which shows that this fabric is able to support a composite interface and display high apparent contact angles $(\theta^* \ge 140^\circ)$ even with octane $(\gamma_{\rm lv} = 21.7 \,{\rm m}{
m N}\,{
m m}^{-1})$. Taking the geometry of the large fiber bundle as the dominant texture $(R_{\rm bundle} = D_{\rm bundle} = 150\,\mu{\rm m},$ $R_{\rm fiber} = 5 \,\mu m$, $D_{\text{fiber}} = 10 \,\mu\text{m}, \ D^* = 6, \ \theta = 55^\circ$), we obtain a value of the robustness factor $A^* = 2.5$ for octane. The measured contact angles on various dip-coated surfaces with selected polar and nonpolar liquids are provided in the Supporting Information. It should be noted, however, that when the equilibrium contact angle θ is <90°, the composite interface is necessarily metastable,^[4,19,20,25,41–43] that is, it corresponds to a local minimum in the overall Gibbs free energy for the system, while the completely wetted Wenzel state corresponds to the global minimum.^[27]

To obtain even higher apparent contact angles with very low surface tension liquids, it is necessary to increase the value of the spacing ratio D^* (see Eq. 4). For fabrics, this can be readily achieved by equi-biaxial stretch-

ing, such that the imposed strain is the same in both directions. Here, strain is defined as $\varepsilon = (L-L_0)/L_0$, where L and L_0 represent the stretched and unstretched dimensions of the surface, respectively. Stretching a fabric sample (such that the interfiber spacing D is increased for a fixed value of the fiber radius R) increases the spacing ratio to $D^*_{\rm stretched} = D^*_{\rm unstretched}(1+\varepsilon)$, leading to an increase in the value of the apparent contact angles. Based on the Cassie–Baxter relation^[23] (Eq. 4), the apparent contact angles on the stretched fabric can then be computed as:

$$\cos \theta^*_{\text{stretched}} = -1 + \frac{1}{D^*_{\text{stretched}}} [\sin \theta + (\pi - \theta) \cos \theta]$$
$$= -1 + \frac{1}{1 + \varepsilon} (1 + \cos \theta^*_{\text{unstretched}})$$
(5)

However, as noted earlier, for a cylindrical geometry the two design parameters D^* and A^* are strongly coupled (see Eq. 3). As a result, increasing the interfiber spacing D causes more severe sagging of the liquid–air interface, leading to lower values of the robustness factor A^* . Thus, with increasing values of D^* , we expect to see initially an increase in the value of apparent contact angles θ^* , followed by a sudden transition to the Wenzel state once A^* decreases to a value close to unity.

The changes in the apparent advancing and receding contact angles for dodecane ($\gamma_{lv} = 25.3 \text{ msm}^{-1}$, $\theta = 70^{\circ}$) on a dip-coated polyester fabric as a function of the applied strain are shown in Figure 4a. As expected from Equation 5, initially there is an increase in both the apparent advancing and receding contact angles with increasing strain, due to the increasing fraction of



Figure 4. a) Apparent advancing (red squares) and receding (blue dots) contact angles for dodecane ($\gamma_{lv} = 25.3 \text{ mN m}^{-1}$) on a dip-coated polyester fabric as a function of the applied biaxial strain. The dashed red and blue lines are the apparent contact angles predicted by Equation 5. b) Predictions for A^{*} (red line) and D^{*} (blue line) as a function of the imposed biaxial strain on the fabric. c) Switchable oleophobicity of the dip-coated fabric with decane ($\gamma_{lv} = 23.8 \text{ mN m}^{-1}$). d,e) Decane droplets on an unstretched and stretched (30% biaxial strain) dip-coated polyester fabric, respectively.

trapped air underneath the liquid droplet. Figure 4b shows the variation with applied strain in the values of both the robustness factor A^* and the spacing ratio D^* for dodecane on the dip-coated fabric surface. Comparing the responses in Figure 4a and b, we see a rapid transition from a composite or Cassie–Baxter interface to a wetted interface with both $\theta^*_{adv} = \theta^*_{rec} \approx 0^\circ$ when $A^* \rightarrow 1$. Threshold values of A^* for the transition from the Cassie regime to the Wenzel regime were measured to be consistently close to unity (varying between $A^* = 1.0$ and $A^* = 1.7$) for various polar and nonpolar liquids. Thus, biaxial stretching provides a simple mechanism for systematically adjusting the wetting properties of the dip-coated polyester fabric. To our knowledge, this is the first demonstration of tunable superoleophobicity on any surface.

An example of switchable oleophobicity of the fabric surface is shown in Figure 4c. When a droplet of decane ($\gamma_{\rm lv} = 23.8 \text{ ms} \text{m}^{-1}$, $\theta = 60^{\circ}$) is placed on an unstretched ($D^* = 6$) dip-coated fabric, the relatively high value of the robustness factor ($A^* = 2.8$) enables the fabric to support a composite interface with the decane droplet, and thereby display high advancing apparent contact angles $\theta^* = 149 \pm 2^{\circ}$ (see Fig. 4d). However, when the fabric is biaxially stretched to a strain of 30% ($D^* = 7.8$), the robustness factor is reduced to almost unity ($A^* \approx 1.4$), and the fabric is fully wetted by the decane, with $\theta^*_{\rm adv} \approx 0^{\circ}$ (see Fig. 4e).

When the strain on the fabric is released, the initial surface texture is restored. Returning to the original value of the interfiber spacing *D* leads once more to high values of the robustness factor A^* . This allows the fabric to once more support a composite Cassie–Baxter interface and display high apparent contact angles with a new droplet of decane placed at any location on its surface, except the wet spot where the initial liquid drop was imbibed. The



fabric is able to regenerate its oleophobic properties at the original wetted spot as well, as after a simple evaporative drying process. The data in Figure 4c show the apparent contact angles with decane at a single fixed location on the dip-coated polyester fabric. The first contact angle measurement is performed on the unstretched fabric. Next, the fabric is stretched until D^* increases to a value of 7.8, and correspondingly A^* decreases to a value of 1.4, leading to complete wetting. The strain is then removed and the fabric is placed in a vacuum oven to dry at 100 °C for 20 min. This is followed by another contact-angle measurement at the same location. Next, the fabric is stretched again, and the cycle is repeated. It is clear from Figure 4c that biaxial stretching enables the fabric to easily switch its wetting characteristics from perfectly oil-wetting to nonwetting easily and reproducibly. Further, EDAXS elemental mapping (see Supporting Information) and microscopy on the dip-coated fabrics after the sixth cycle indicate that there is no apparent degradation in the fluorodecyl POSS coating after repeated stretching. Similar switchable wettability can also be achieved with ethanol ($\gamma_{lv} = 22.1 \text{ m} \text{ m} \text{ m}^{-1}$), methanol $(\gamma_{lv} = 22.7 \text{ mn m}^{-1})$, and dodecane $(\gamma_{lv} = 25.3 \text{ mn m}^{-1})$ by stretching up to 20, 30, and 60% strain, respectively (see Supporting Information for data on switchable wettability with methanol).

From the definitions of the design parameters A^* and D^* in Equations 3 and 4, it is clear that for the same value of the spacing ratio D^* , different liquids possess different values of the robustness factor A^* , due to differing values of surface tension, capillary length, and equilibrium contact angle for each liquid on the fluorodecyl POSS-coated surface. Thus, while the dip-coated fabric may support a composite interface with a particular contacting liquid ($A^* >> 1$), another liquid with a lower surface tension may fully wet the fabric ($A^* \approx 1$). In addition, as shown in Figure 4b, biaxial stretching of the fabric provides a simple mechanism to tune the robustness factor A^* and correspondingly adjust the conditions under which a liquid will wet and permeate into the fabric, or remain beaded up on the surface.

Figure 5 highlights the strain-induced sequential wetting of a dip-coated polyester fabric with a series of different liquid drops by exploiting this sensitivity to the surface tension and equilibrium contact angle of the contacting liquid. The unstretched dip-coated fabric shown in Figure 5a ($D^* = 6$) is able to support a composite interface with four different low-surface-tension alkanes: octane ($\gamma_{lv} = 21.7 \text{ m} \text{ m}^{-1}$), decane ($\gamma_{lv} = 23.8 \text{ mN m}^{-1}$), dodecane ($\gamma_{lv} = 25.3 \text{ mN m}^{-1}$), and hexadecane ($\gamma_{lv} = 27.5 \text{ m}\text{m}\text{m}^{-1}$). Starting from this initial state, we continuously increase the applied strain on the fabric. At a strain of 15%, the spacing ratio reaches a value of $D^* = 6.9$, and the lowest-surface-tension oil (octane, $A^*_{\rm octane} \approx 1.7$) transitions to a fully wetted Wenzel state (Fig. 5b), while the other three liquids maintain a Cassie-Baxter composite interface with the dip-coated fabric. Thus, the stretched fabric can demonstrate remarkably different wetting properties with liquids having a surface tension difference of only $\Delta \gamma_{lv} \sim 2 \, m_N \, m^{-1}$ between them. Additional strain increases the spacing ratio further, and once it reaches a value of $D^* = 7.8$, the decane droplet ($A^*_{decane} \approx 1.4$) wets the fabric surface (Fig. 5c), while dodecane and hexadecane still maintain a nonwetting composite interface. Further stretching of the fabric (until $D^* = 9.6$) causes even the dodecane droplet $(A^*_{\text{dodecane}} \approx 1.0)$ to be imbibed into the fabric (Fig. 5d).

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Figure 5. Sequential wetting of four alkane droplets on a dip-coated polyester fabric. a) Super-repellency of the unstretched, dip-coated, fabric against octane ($\gamma_{lv} = 21.7 \text{ mN m}^{-1}$, $\theta = 55^{\circ}$), decane ($\gamma_{lv} = 23.8 \text{ mN m}^{-1}$, $\theta = 60^{\circ}$), dodecane ($\gamma_{lv} = 25.3 \text{ mN m}^{-1}$, $\theta = 70^{\circ}$) and hexadecane ($\gamma_{lv} = 27.8 \text{ mN m}^{-1}$, $\theta = 78^{\circ}$). b) At 15% strain, the octane droplet transitions to the Wenzel regime with $A^*_{\text{octane}} = 1.7$. c) At 30% strain, the decane droplet transitions to the Wenzel regime with $A^*_{\text{decane}} = 1.4$. d) At 60% strain, the dodecane droplet transitions to the Wenzel regime with $A^*_{\text{dodecane}} = 1.0$. The hexadecane droplet does not transition into the Wenzel regime until the woven fabric starts to tear apart, at ~70% strain.

In conclusion, in this work we have developed a simple and benign dip-coating process that enables us to provide a flexible and conformal coating of extremely low-surface-energy fluorodecyl POSS molecules on any surface, including those that inherently possess re-entrant textures, such as duck feathers, lotus leaves, or commercially available fabrics. The synergistic effect of roughness, re-entrant topography of the substrate, and the low surface energy of fluorodecyl POSS molecules enables the dip-coated surfaces to support a composite interface even with very-low-surface-tension liquids. We have also used two design parameters D^* and A^* to provide an a priori estimate of both the apparent contact angles as well as the robustness of the composite Cassie-Baxter interface. The design framework outlined in this paper enables us to identify and develop suitably textured surfaces that can have their surface-wettability characteristics systematically adjusted. By combining this understanding with a dip-coating process that provides a conformal and flexible fluorinated coating, we can reversibly switch the wettability behavior of fabric surfaces between superwetting and superrepellent with a wide range of polar and nonpolar liquids using simple mechanical deformation. Biaxial stretching of a dipcoated, commercial polyester fabric can cause an appreciable increase in both the apparent advancing and receding contact angles, as predicted by changes in the spacing ratio D^* . As a result of the strong coupling between the two design parameters A^{*} and D^* for a typical woven fibrous geometry, stretching commercial fabrics also leads to a dramatic reduction in the robustness of the composite interface that is supported with a given contacting liquid. Indeed, beyond a critical strain (at which the robustness A^{*} decreases to values close to unity), the contacting liquid



spontaneously penetrates the fabric texture, leading to near-zero contact angles. However, because of the conformal and flexible characteristics of the fluorodecyl POSS coating, mechanical unloading and drying of the fabric enables the super-repellency of the sample to be repeatedly regained.

Experimental

Dip-coating: For the dip-coating process, we first prepare a solution of fluorodecyl POSS (50 wt%) and Tecnoflon (BR9151) in Asahiklin AK-225 (Asahi glass company) at an overall solid concentration of 10 mg mL⁻¹. Tecnoflon is a commercial fluoro-elastomer manufactured by Solvay-Solexis. The use of Tecnoflon as a polymeric binder prevents the crystallization of fluorodecyl POSS, and yields a more conformal and elastomeric coating. Next, the substrate to be dip-coated is immersed in the fluorodecyl POSS-Tecnoflon solution. After 5 min, the substrate is removed from the solution and placed to dry in a vacuum oven for 30 min at a temperature of 60° C.

Biaxial Stretching: The fabric-stretching experiments were carried out using a custom built biaxial stretcher. Multiple markings were made on the fabric surface, with an intermarking separation of 5 mm on the unstretched fabric. Next, as the fabric was stretched, we measured the separation between the markings to provide an accurate measurement of strain.

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 μ L) onto 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 $\sim 2^\circ$.

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