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A number of surfaces encountered in nature are superhydrophobic, displaying water contact angles (WCA) > 150°, and low contact angle hysteresis. The most widely-known example of a superhydrophobic surface found in nature is the surface of the lotus leaf. It is textured with small 10-20 micron sized protruding nubs which are further covered with nanometer size epicuticular wax crystalloids.¹ Numerous studies have shown that it is this combination of surface chemistry plus roughness on multiple scales – micron and nanoscale that imbues super hydrophobic character to the lotus leaf surface. The question we seek to answer is whether it is also possible through control of surface chemistry and morphology to create surfaces which show comparable levels of oil-repellency.

Two distinct models, developed by Cassie² and Wenzel,³ are commonly used to explain the effect of roughness on the apparent contact angle of a drop sitting on a surface. The Wenzel model recognizes that surface roughness increases the available surface area of the solid, which geometrically increases the contact angle for the surface according to:

$$\cos \theta^* = r \cos \theta \quad (1)$$

here θ^* is the apparent contact angle, r is the surface roughness, and θ is the equilibrium contact angle on a smooth surface of the same material. The Cassie model on the other hand proposes that the superhydrophobic nature of a rough surface is caused by air remaining trapped below the water droplet. Thus, the contact angle is an average between the value of the fluid-air contact angle (i.e. 180°) and the equilibrium solid-liquid value on a smooth surface (θ). If ϕ_s is the fraction of the solid in contact with water, the Cassie equation yields:

$$\cos \theta^* = -1 + \phi_s (1 + \cos \theta) \quad (2)$$

Thermodynamic arguments can be used to determine whether a rough hydrophobic surface will stay in the Wenzel or the Cassie state (for a good discussion see the work of Marmur⁴). Previous work has shown that if we consider a series of substrates with progressively increasing equilibrium contact angles, a transition from the Wenzel to the Cassie state should ultimately be observed on the corresponding rough surfaces⁵ The threshold value of the critical equilibrium contact angle (θ_c) for this transition can be obtained by equating eqns. 1 and 2:

$$\cos \theta_c = (\phi_s - 1) / (r - \phi_s) \quad (3)$$

Because $r > 1 > \phi_s$ the critical angle θ_c is necessarily greater than 90°, and thus we require $\theta > 90^\circ$ to create superhydrophobic surfaces. This is readily achievable using siloxanes or fluorinated surfaces and a wide variety of superhydrophobic surfaces have now been created. However, these arguments also explain why researchers so far have not been successful in making super-oleophobic surfaces, i.e. surfaces with contact angles > 150° for mobile alkane oils such as decane ($\gamma = 23.8$ mN/m) or octane ($\gamma = 21.6$ mN/m). For a smooth surface to have an equilibrium contact angle > 90° with a liquid alkane, the surface would need to have a surface energy < 5 mN/m (based on the work of Shibuchi et al.⁶). Zisman et al.⁷ reported that the surface free energy decreased in the order $-\text{CH}_2 > -\text{CH}_3 > -\text{CF}_2 > -\text{CF}_2\text{H} > -\text{CF}_3$,^{7,8} and the lowest solid surface energies reported to date are in the range of ~6 mN/m (for a hexagonally closed pack arrangement of $-\text{CF}_3$ groups on a surface).^{7,8}

Recent work in our laboratories has led to the development of a new class of hydrophobic POSS molecules in which the rigid silsesquioxane cage is surrounded by fluoroalkyl groups. A number of different molecules with different organic groups (including 1H,1H,2H,2H-heptadecafluorodecyl (referred to as fluorodecyl POSS); 1H,1H,2H,2H-tridecafluorooctyl (fluorooctyl POSS) have now been synthesized, and this class of materials is denoted generically as fluoroPOSS. The fluoroPOSS molecules contain a very high surface concentration of fluorine containing groups, including $-\text{CF}_2$ and $-\text{CF}_3$ moieties. The high surface concentration and surface mobility of these groups, as well as the relatively high ratio of $-\text{CF}_3$ groups with respect to the CF_2 groups results in one of the most hydrophobic and lowest surface energy materials available today.⁹

By varying the mass fraction of fluoroPOSS dispersed in various polymers, we can systematically change the surface energy of the polymer-fluoroPOSS blend. This ability affords us unusual control over the equilibrium contact angle of the blends and provides us with a mechanism for systematically studying the transition from the Wenzel to the Cassie state on model rough surfaces. In the present work, we study blends of a moderately hydrophilic polymer, poly(methyl methacrylate) (PMMA, $M_w = 540$ kDa, PDI ~ 2.2) and fluorodecylPOSS as a model system. The smooth surfaces (maximum rms roughness of ~ 4.4 nm; maximum advancing water contact angle = 123°) are created by spin coating, and the rough surfaces are created by electrospinning¹⁰ solutions of fluorodecyl POSS and PMMA from Asahiklin-AK225 (Asahi Glass Co.) solvent.

Fig. 1a shows a plot of the apparent contact angle θ_{apparent} on the rough electrospun surface shown in Figure 1b as the equilibrium contact angle θ of the corresponding smooth (spin coated) surface is varied by changing the blend composition. It can be seen that the transition from the Cassie to the Wenzel state for these systems does not occur as the contact angle is progressively reduced to 90°. It is thus possible to generate very hydrophobic rough surfaces, with high advancing contact angles, even though their corresponding smooth surfaces are hydrophilic! However, these

textured surfaces exhibit high contact angle hysteresis. Liquid droplets deposited on the fiber surfaces are trapped in a nonwetting state, as they advance, due to the severe surface curvatures of the electrospun fibers (with diameters 100 – 500nm). For low POSS concentrations (< 2 wt%) the re-entrant surfaces of the fibers results in high advancing contact angles,¹¹ indicative of being in the Cassie state, however, this Cassie state is metastable. The transition energy between the Cassie and Wenzel states increases with the concentration of POSS and the electrospun fiber mat becomes truly superhydrophobic (with advancing and receding contact angles of $161\pm 2^\circ$) for all POSS concentrations above 10 wt%. Furthermore, these electrospun surfaces are also strongly oleophobic (with advancing contact angles > 140° and receding contact angles > 100° for Octane), even though corresponding spin-coated surfaces are oleophilic at all fluorodecyl POSS concentrations.

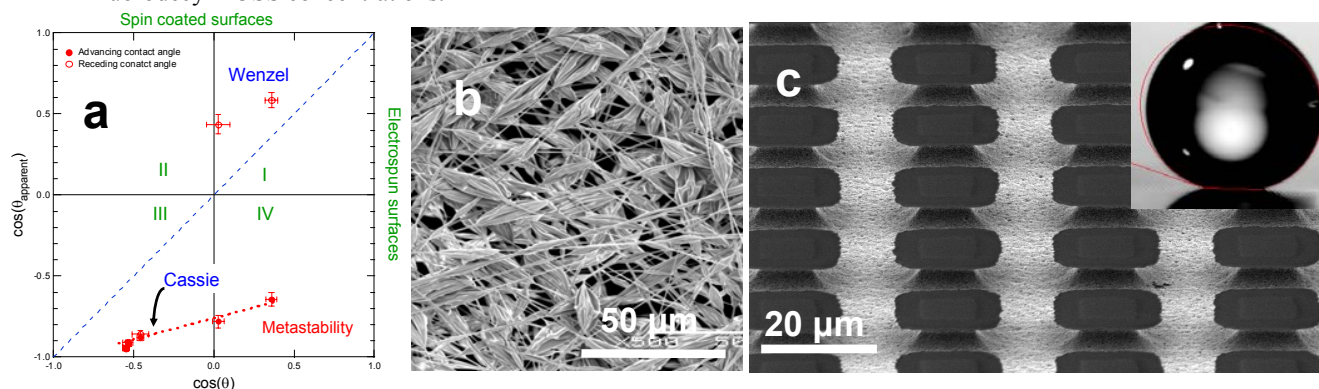


Figure 1a. Advancing and receding contact angles on the electrospun (rough) PMMA + fluorodecyl POSS surfaces as a function of the equilibrium contact angles measured on smooth spin-coated surfaces. **b.** An SEM micrograph of the electrospun surfaces. **c.** An SEM micrograph of the SiO₂ micropillars. The inset shows a drop of octane on a silanized micropillar surface with inter-pillar spacing of 40 μm.

To demonstrate the importance of re-entrant curvatures in the electrospun fiber mats, we also fabricated model SiO₂ micropillars with large flat caps (Fig. 1c) using lithographic chemical etching. A number of different pillar surfaces with inter-pillar spacing varying between 10 μm – 40 μm were fabricated, in order to vary the fractional surface coverage ϕ_s . The pillar height and cap width were held fixed at 7 and 20 μm respectively. The capped pillars were then treated with vapor phase tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane, to lower the substrate surface energy chemically. The inset on Fig. 1c shows a drop of octane on a silanized micropillar surface (advancing contact angle ~ 163° , receding contact angle ~ 145°). These contact angles are the highest ever reported for octane on any surface. Corresponding measurements of the equilibrium contact angle for octane on a smooth SiO₂ surface covered with the same silane coating give $\theta \sim 55^\circ$. Additional measurements show that octane droplets on these model pillar surfaces exist in a metastable state.

Conclusions

This work outlines the systematic creation of super-hydrophobic and super-oleophobic surfaces. Electrospun fiber mats containing as little as 2 wt% POSS are strongly hydrophobic, even though spin coated surfaces with the same fluorodecylPOSS/PMMA composition remain hydrophilic. At higher concentrations of the fluorodecylPOSS it is also possible to create highly oleophobic substrates with low contact angle hysteresis; however these surfaces are metastable. The critical role of re-entrant surface curvature in controlling the ability to generate Cassie surface states is demonstrated by lithographically fabricating a model surface of capped pillars covered with a fluorosilane chemical coating.

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