

ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201202554

**Hierarchically Structured Superoleophobic Surfaces with
Ultralow Contact Angle Hysteresis**

*Arun K. Kota, Yongxin Li, Joseph M. Mabry, and Anish
Tuteja**

Supporting Information for Hierarchically structured superoleophobic surfaces with ultra-low contact angle hysteresis

By *Arun K. Kota, Yongxin Li, Joseph M. Mabry, and Anish Tuteja**

[*] Prof. A. Tuteja, Dr. Arun K. Kota, Yongxin Li
Department of Materials Science and Engineering
University of Michigan, Ann Arbor, MI, 48109 (USA)
E-mail: atuteja@umich.edu

Dr. J. M. Mabry
Rocket Propulsion Division
Air Force Research Laboratory, Edwards Air Force Base, CA, 93524 (USA)

Section 1. Table of contact angles.

Table S1 lists the various polar and non-polar liquids used in this study and their advancing and receding contact angles on silicon wafer spin-coated with 50 wt% fluorodecyl POSS + PMMA blend and stainless steel mesh 70 coated with electrospun microbeads of 50 wt% fluorodecyl POSS + PMMA blend. Note that some of the liquids (represented by a “*” in Table S1) display low receding contact angles because these liquids are good solvents for PMMA.

Table S1. The advancing and receding contact angles of various polar and non-polar liquids used in this study on silicon wafer spin-coated with 50 wt% fluorodecyl POSS + PMMA blend and stainless steel mesh 70 ($D_{fiber}^* = 1.4$) coated with electrospun microbeads of 50 wt% fluorodecyl POSS + PMMA blend.

Liquid	Surface tension	θ_{adv}	θ_{rec}	θ_{adv}^*	θ_{rec}^*
<i>n</i> -Heptane	20.1	61°	38°	155°	151°
Methanol	22.7	53°	8°	154°	150°
5% water + 95% methanol	23.4	71°	16°	155°	151°
Cyclohexane	24.9	72°	45°	156°	152°
Acetone*	25.2	42°	4°	0°	0°
<i>n</i> -Dodecane	25.3	72°	50°	159°	155°
15% water + 85% methanol	25.3	78°	64°	156°	152°
<i>n</i> -Butanol	26.3	55°	11°	158°	154°
Tetrahydrofuran*	26.4	24°	4°	0°	0°
Chloroform*	27.5	20°	4°	0°	0°
<i>n</i> -hexadecane	27.5	79°	57°	160°	157°
25% water + 75% methanol	27.5	82°	70°	159°	156°
Toluene*	28.0	31°	5°	155°	126°
Benzene*	28.8	39°	6°	154°	128°
Cyclopentanol	33.2	63°	16°	160°	157°
50% water + 50% methanol	34.7	93°	79°	163°	160°
Dimethylformamide*	35.6	36°	5°	153°	96°
Rapeseed oil	35.7	89°	66°	164°	161°

Dimethyl Sulfoxide*	43.5	101°	6°	160°	112°
75% water + 25% methanol	47.2	115°	97°	163°	161°
85% water + 15% methanol	51.3	119°	98°	165°	163°
95% water + 5% methanol	62.9	122°	103°	165°	163°
Water	72.1	123°	113°	166°	165°

Section 2. Prediction of droplet roll-off angles.

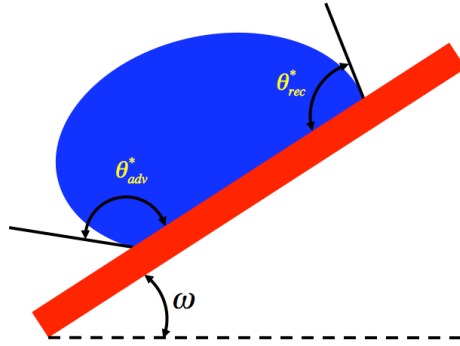


Figure S1. A schematic illustrating a drop on a textured surface tilted at an angle ω relative to the horizontal.

Consider a liquid droplet on a textured surface tilted at an angle ω relative to the horizontal (see **Fig. S1**). The droplet forms an apparent advancing contact angle θ_{adv}^* and an apparent receding contact angle θ_{rec}^* at the leading and the trailing edges along the solid surface, respectively. Balancing the work done by the droplet descending under gravity with the work done in wetting the solid surface at the leading edge the droplet and the work done in dewetting from the solid surface at the trailing edge of the droplet, Furmidge^[1] derived a relation for the roll-off angle ω as:

$$\sin \omega = \frac{\gamma_{lv} D_{TCL} (\cos \theta_{rec}^* - \cos \theta_{adv}^*)}{\rho g V} \quad (S1)$$

Here, ρ and γ_{lv} are the density and surface tension of the liquid, respectively, g is the acceleration due to gravity, V is the volume of the droplet, and D_{TCL} is the width of the triple

phase contact line perpendicular to the rolling direction. When the contact angle hysteresis is low, as is the case on our hierarchically structured surfaces, the shape of the droplet does not deviate significantly from a spherical cap. In such cases, the width of the triple phase contact line can be computed as:^[2]

$$D_{TCL} = 2 \cos\left(\bar{\theta}^* - \frac{\pi}{2}\right) \left[\frac{3V}{\pi(2 - 3\cos\bar{\theta}^* + \cos^3\bar{\theta}^*)} \right]^{\frac{1}{3}} \quad (\text{S2})$$

Here, $\bar{\theta}^*$ is the average apparent contact angle, given as:

$$\cos\bar{\theta}^* = \frac{\cos\theta_{adv}^* + \cos\theta_{rec}^*}{2} \quad (\text{S3})$$

Our experimentally measured roll-off angles match reasonably well with those predicted by equations (S1)-(S3).

References.

- [1] C. G. Furmidge, *J. Coll. Sci.* **1962**, *17*, 309.
- [2] W. Choi, A. Tuteja, J. M. Mabry, R. E. Cohen, G. H. McKinley, *J. Colloid Interf. Sci.* **2009**, *339*, 208.

Movie Legends

Movie S1. This video illustrates the roll-off of *n*-hexadecane droplets on our hierarchically structured superoleophobic surface (stainless steel mesh 70 coated with electrospun microbeads of 50 wt% fluorodecyl POSS + PMMA blend) that is tilted at an angle 3° relative to horizontal. *n*-hexadecane is dyed red.

Movie S2. This video illustrates the roll-off of *n*-heptane droplets on the hierarchically structured superoleophobic surface (stainless steel mesh 70 coated with electrospun microbeads of 50 wt% fluorodecyl POSS + PMMA blend) that is tilted at an angle 3° relative to horizontal.

Movie S3. This video illustrates the bouncing of a $2\ \mu\text{L}$ *n*-hexadecane droplet that is dropped on the hierarchically structured superoleophobic surface (stainless steel mesh 70 coated with electrospun microbeads of 50 wt% fluorodecyl POSS + PMMA blend) from a height 3 mm above the surface. The surface is tilted at an angle 2° relative to horizontal. The video is captured at 1800 frames per second.

Movie S4. This video illustrates the bouncing of a $2\ \mu\text{L}$ *n*-heptane droplet that is dropped on the hierarchically structured superoleophobic surface (stainless steel mesh 70 coated with electrospun microbeads of 50 wt% fluorodecyl POSS + PMMA blend) from a height 3 mm above the surface. The surface is tilted at an angle 2° relative to horizontal. The video is captured at 1800 frames per second. The deformation in the shape of the *n*-heptane droplet during bouncing is significantly greater than that of the *n*-hexadecane droplet because of the lower values of surface tension and viscosity for *n*-heptane.