Supporting Information: Delayed lubricant depletion of Slippery Liquid Infused Porous Surfaces using precision nanostructures

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Table of Content

Supporting Tables

Table S1 – Etching times and deposition thickness for nanostructure generation

Sample	**SiO_2 thickness / nm**	**O_2 etch / s**	**CHF_3/Ar etch / min**	**Cl_2 etch / min**	***t* ALD / nm**	**Cl_2 etch / min**
Nanoholes	200	5	9	10	N/A	N/A
Nanopillars	200	5	6	10	N/A	N/A
Nanotubes	200	5	9	5	30	10

Table S2 – Oxford RIE etching conditions for SiO_2 mask etching

Oxford RIE conditions – capacitively coupled plasma				
Oxygen breakthrough	**Pressure / mTorr**	**RF Power / W**	**O_2 / sccm**	
	50	100	50	
SiO_2 etch	**Pressure /mTorr**	**RF Power / W**	**CHF_3 / sccm**	**Ar /sccm**
	50	200	12	38

Table S3 – STS etching conditions for Si etching

ASE, STS MESC Multiplex conditions – inductively coupled plasma								
Sample	**1st Si etch**				**2nd Si etch**			
	Coil /W	Platen /W	P /mTorr	t /min	Coil /W	Platen /W	P /mTorr	t /min
Nanoholes	300	40	3	10	N/A	N/A	N/A	N/A
Nanopillars	300	100	3	10	N/A	N/A	N/A	N/A
Nanotubes	500	200	3	5	300	100	3	10

Table S4 – Interfacial energy values

	Surface tension / mN/m
(Krytox 1525)[1] γ_L	19
(DI water) γ_W	72.2
Krytox-Water γ_{LW}[1]	50.5

Supporting Text

Text S1 – Critical roughness

Based on the surface energy balance, there is a minimum surface roughness required for a thermodynamically stable configuration which is predicted by:[2]

$$R > \frac{\gamma_{LW}}{\gamma_L cos\theta_L - \gamma_W cos\theta_W} \quad \text{[Eq. S1]}$$

For the case of a water droplet and Krytox 1525, the threshold value to support a stable SLIPS is $R > 1.2$.

Text S2 – Thermodynamic stability of lubricant film

The stability of a lubricant film under static conditions can be assessed by considering the interfacial energy of the solid that is fully wetted either by water (E_W) – the only immiscible liquid tested in this paper, or the lubricant with (E_{LW}) or without (E_L) a water droplet atop of the lubricant:[2]

1. Lubricant wets the solid with water present

$$E_{LW} = R\gamma_{SL} + \gamma_{LW} + \gamma_W \quad \text{[Eq. S2]}$$

2. Lubricant wets the solid without water present

$$E_L = R\gamma_{SL} + \gamma_L \quad \text{[Eq. S3]}$$

3. Water wets the solid

$$E_W = R\gamma_{SW} + \gamma_W \quad \text{[Eq. S4]}$$

where R is the roughness ratio and γ_{SL}, γ_{LW}, γ_L and γ_W represent the surface energies of the solid-lubricant interface, lubricant-water interface, lubricant-air and water-air interface, respectively.

To ensure water does not wet the solid, E_W must be in a higher energy state than E_{LW}, we therefore write E_W - E_{LW} > 0, which further expands to:

$$R(\gamma_{SW} - \gamma_{SL}) - \gamma_{LW} > 0 \qquad \text{[Eq. S5]}$$

To reduce this to measurable quantities, we can use Young's equation to obtain

$$R[(\gamma_S - \gamma_W cos\theta_W) - (\gamma_S - \gamma_L cos\theta_L)] - \gamma_{LW} > 0 \qquad \text{[Eq. S6]}$$

which can be simplified to:

$$\Delta E_{LW} = R(\gamma_L cos\theta_L - \gamma_W cos\theta_W) - \gamma_{LW} > 0 \qquad \text{[Eq. S7]}$$

The same approach is taken for ΔE_L to obtain:

$$\Delta E_L = R(\gamma_L cos\theta_L - \gamma_W cos\theta_W) - \gamma_W - \gamma_L > 0 \qquad \text{[Eq. S8]}$$

where θ_L and θ_W are the Young's contact angles of the lubricant and water on the solid surface.

Text S3 - Spreading coefficient of Krytox 1525 on water

Krytox is commonly used in SLIPS surfaces, by virtue of its immiscibility with water. However, to determine whether it is energetically favourable for Krytox to spread on water, the spreading coefficient is calculated by the following equation:

$$S_{LW} = \gamma_W - (\gamma_L + \gamma_{WL}) \qquad \text{[Eq. S9]}$$

Based on the values in Table S4, S_{LW} is calculated to be 2.704, indicating it is energetically favourable to spread on water, thus giving rise to cloaking. The ramifications of cloaking are discussed elsewhere,[1] however as the aim is to compare the effect of nanostructure on performance rather than lubricant, it is not considered pertinent.

References

(1) Sett, S.; Yan, X.; Barac, G.; Bolton, L. W.; Miljkovic, N. Lubricant-Infused Surfaces for Low-Surface-Tension Fluids: Promise versus Reality. *ACS Appl. Mater. Interfaces* **2017**, *9* (41), 36400–36408.

(2) Wong, T.-S. S.; Kang, S. H.; Tang, S. K. Y. Y.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J. Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity. *Nature* **2011**, *477* (7365), 443–447.