Superhydrophobic-Superhydrophilic Binary Micropatterns by Localized Thermal Treatment of Polyhedral Oligomeric Silsesquioxane (POSS)-Silica Films

Thomas M. Schutzius, Ilker S. Bayer, Gregory M. Jursich, Arindam Das,

and Constantine M. Megaridis

Supporting Information

The photographs shown in **Fig. S1** show the heat-induced change in wettability from superhydrophobic to superhydrophilic. Figure S1a shows three droplets beaded on a superhydrophobic MSQ-HFS coating applied on an aluminum plate. Figure S1b shows the flame treatment using a propane torch; open-air exposure lasted only a few seconds. The flame was operated in the premixed mode, thus assuring the absence of carbonaceous soot (as also affirmed by the blue color of the flame). After flame treatment, the MSQ-HFS coating became superhydrophilic, as shown in Fig. S1c, d and e.

In the case of a semi-infinite solid medium heated on a spot, the corresponding rise in surface temperature (ΔT) can be estimated using the following expression

$$\Delta T(t) = \frac{(1-R)I}{K} \left(\frac{\delta}{\sqrt{\pi}} - \frac{1}{\alpha} \left(1 - e^{(\alpha \delta/2)^2} \operatorname{erfc}(\alpha \delta/2) \right) \right)$$
(S1)

where *R* is the surface reflection coefficient, *I* the irradiance (uniform surface source), *K* the thermal conductivity, δ the diffusion length ($\delta = 2\sqrt{\kappa t}$; with κ being the thermal diffusivity and *t* the time), and α the absorption coefficient.^{1, 2} With R = 0.05, K = 0.01 W cm⁻¹ K⁻¹, $\kappa = 6 \times 10^{-3}$ cm² s⁻¹, $\alpha = 10^{3}$ cm⁻¹

for glass,² and $I \approx 0.2$ MW cm⁻², **Eq. S1** predicts that $\Delta T \sim 2,000$ K after only t = 0.022 ms, a temperature that is comparable with the propane flame temperature.

Figure S4a-c, Peak 1 and Peak 2 correspond to Si-R and Si-O bonding, respectively. After thermal treatment, an increase in Peak 2 is observed with a corresponding decrease in Peak 1, which can be interpreted as an increase in Si-O bonding with a decrease in hydrophobic groups, i.e., increased hydrophilicity. **d-f**, Peak 1 corresponds to Si-O bonding, and its concentration increases from **d** to **e** and **f**, suggesting increased hydrophilicity of the coating. **g-i**, Peak 1 corresponds to adventitious carbon and/or simple C-H / C-C bonds. Its reduction from **g** to **h** and **i** is indicative of suspected cleavage of methyl groups, and increased hydrophilicity.

Figure S6a-b presents two SEM micrographs with increasing magnification from a to b of a spraydeposited MSQ-HFS coating (1.0 MSQ/HFS mass ratio) after flame treatment. This coating displayed superhydrophilic behavior. It is apparent that the primary morphological features of the flame-treated coating remain relatively unchanged as compared with the untreated coating (Fig. 1).

Supplementary References

- 1. M. von Allmen, Laser-Beam Interactions with Materials, Spinger-Verlag, Berlin, 1987.
- G. Allcock, P. E. Dyer, G. Elliner and H. V. Snelling, *Journal of Applied Physics*, 1995, 78, 7295-7303.



Figure S1. (a) Photograph of beaded water droplets on a MSQ-HFS film applied on an aliminum plate. (b) Flame treatment of the coating shown in (a) using a propane torch for a few seconds from a distance of 5-10 cm. (c) Photograph of the flame-treated coating just before depositing a water droplet (~10 μ L). (d) Completely wetting droplet spreading on the flame-treated coating. (e) Completely wetting droplet at its final fully-spread state.



Figure S2. Superhydrophobic MSQ-HFS coatings patterned with a single pass of a CO_2 laser beam at a fixed power (1.0 W) and speed (2.0 cm s⁻¹) with a constant focal length and variable distance between the lens and the substrate. The inset scale bars are 100 µm. The distance between the laser and the substrate is decreasing from (a) to (k) (i.e., (a) has the largest distance between the lens and substrate; (k) has the smallest distance between the lens and substrate). The optimum range is between (e)-(h) with the minimum line width in (g) being 109±6 µm. Inset scale bars in the images are all 100 µm.

IC UIC IIT UIC IIT UIC IIT II IIT UIC п UIC UIC п п IIT UIC I III UII II п . II UIC т ПЛ IT UI П 1 TT IIT UIC IIT LV. IIT τ TII UT UIC IIT UIC IIT O. Т T 110 UIC пт IT . IIT UIC IIT UIC IIT UIC IIT UIC IIT UIC п UIC П п UIC IIT UIC IIT UIC IIT IIT

Figure S3. Superhydrophobic MSQ-HFS film deposited onto two quartz substrates (2.54 cm dia.) before (right) and after (left) laser processing, which induces hydrophilicity and increases transparency. A water droplet has been deposited on each surface, but is visible as a bead only on the superhydrophobic disk (right). The droplet on the superhydrophilic disk (left) has fully spread, thus becoming indistinguishable.



Figure S4. XPS data of untreated (superhydrophobic) and heat-treated (superhydrophilic) MSQ-HFS coatings. (a)-(c) Si 2p region; (d)-(f) O 1s region; (g)-(i) C 1s region. Figures in the left column represent untreated state, while figures in the middle and right columns are the corresponding thermally treated states. Thermal treatment was performed by either a flame ((b), (e) and (h)) or CO_2 laser ((c), (f) and (i)). For a given region, each peak is designated by a number.





(b)



Figure S5. Image sequence demonstrating the super-wetting behavior of water on laser patterned areas of the MSQ-HFS coating for (a)-(b) room temperature conditions (T=25°C), and (c)-(d) T=138°C. The time difference from (a) to (b) is 1.0 s, and from (c) to (d) is 0.4 s. Images were captured with a high speed camera mounted overhead at a frame rate of 250 s⁻¹. The size of the laser patterned areas is 6.4 cm^2 ; water droplet volumes are smaller than 10 μ L.



Figure S6. SEM micrographs of spray deposited MSQ-HFS coatings (1.0 HFS/MSQ mass ratio) with increasing magnification left-to-right after flame treatment (i.e., superhydrophilic coating).