

Supporting Information

Why Are Water Droplets Highly Mobile on Nanostructured Oil-Impregnated Surfaces?

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S1. IR Transmission Profiles of SLIPS Samples

Both visible and IR beams need to penetrate the silica prism and the SLIPS film to reach the interface. Since the detected SFG signal is dependent on the intensities of the input laser beams incident on the interface, the absorption of the input visible and IR laser beams before reaching the interface could cause errors in the SFG data. It is well known that IR grade silica prism would not absorb either visible or mid IR beams in the frequency region for this experiment, and the thin SLIPS sample is visibly transparent. Therefore, the thin film does not absorb the visible input beam. Here we want to test whether the thin SLIPS sample absorbs mid IR beam.

Both SLIPS systems have minimal IR absorptions in the frequency region used for this study (Fig. S3), suggesting that the detected SFG signals from the SLIPS/water interface would not be interfered by the possible attenuation of the input laser beams before reaching the SLIPS/water interface. Therefore, we conclude that the SFG signal intensities presented in this research are completely dependent on the orientations of water molecules at the investigated interfaces.

S2. Water SFG Signal Double-band Assignments

We believe that the broad O-H stretching signals with dominated 3200 cm^{-1} peak and 3400 cm^{-1} shoulder shown in Figs. 2a and 2e are contributed by interfacial water molecules with different hydrogen bonding environments, instead of vibrational coupling¹⁻⁵. To confirm this hypothesis, we conducted water isotopic dilution experiments for silicone oil/water and fluorinated oil/water interfaces. Water was mixed with heavy water (deuterium oxide, D_2O) at H_2O -to- D_2O = 1:3 v/v to prepare the isotopically diluted water. SFG spectra were collected from the oil/isotope diluted water interface (Fig. S4). The signal fits well with two water peaks as can be seen in Fig. S4. Although both spectra in Fig. S4 can also be fitted with only one water peak, the obtained fitting results with two peaks are slightly better. Therefore, the original broad O-H signals shown in Fig. 2a and 2e should be contributed by interfacial water molecules in different hydrogen bonding environments in our signal analysis.

S3. Importance of Lubrication Oil in SLIPS

SLIPS are nature-inspired composite material designs consisting of both the solid substrate and the liquid lubrication oil. Our experiments show that lubrication oil alone cannot lead to weak interfacial hydrogen bonding interactions. Indeed, nanostructuring plays a significant role in reducing intermolecular interactions at the liquid/liquid interface. To better understand the role of lubrication film on interfacial forces and molecular ordering at the liquid/liquid interface, we conducted experiments on nanostructured functionalized (silicone and fluorinated-polymer) surfaces without lubrication. For this experiment, SFG spectra were collected from the solid/liquid interface of a water droplet residing on the nanostructured surface without lubrication. As shown in Fig. S5(a) for fluorinated surface and Fig. S5(b) for silicone compatible surface, very strong SFG water O-H stretching signals were detected. This is in stark contrast with the SFG signals obtained from a nanostructured lubricated water/oil interfaces (Fig. 2b, f). The distinctively different SFG signals in the presence and absence of lubrication oil demonstrate that the lying-down orientation of interfacial water molecules on SLIPS and weak water/oil interfacial interactions are not caused by the nanostructured substrates alone. The lubrication oil plays an important role in determining the interfacial water behavior at the water/oil interface, giving nanostructured lubricated surfaces their signature water repellency.

There is a possibility that SFG signal difference between the oil/water interface (Fig. 2a and 2e) and SLIPS/water interface (Fig. 2b and 2f) is caused by the roughness/scattering of the nanostructure in SLIPS. Such roughness/scattering may reduce the SFG signals from the SLIPS/water interface. However, Fig. S5 shows that very strong SFG water signals were detected from the bare nanostructured substrate/water interfaces, without the lubrication films. Therefore, the scattering effect is unlikely to be the cause of the extremely weak SFG signals from the SLIPS/water interface. Had that been the case, we would have observed weak, scattered signals from these two interfaces unlike the signal in Fig. S5.

S4. SFG Signal Assignment and Discussion About Scattering Effect

In order to further rule out the above possible scattering effect, we conducted additional experiments to prove that the low water SFG signals on SLIPS are due to molecular orientation instead of roughness/scattering. First, we used bulk silicone oil (10 cSt) to contact the nanostructured silicone solid substrate, forming a sample with a thick oil layer (Schematic shown in Figure S6a). SFG signal was then collected from this sample with the input laser beams shining on the sample from top. The collected spectrum is shown in Figure S6a (the black spectrum). Two peaks were observed at 2920 cm^{-1} and 2965 cm^{-1} , corresponding to the silicone methyl symmetric and asymmetric stretching modes respectively. We then drained the excess oil to create the silicone SLIPS sample (the schematic shown in Figure S6b). SFG spectrum was again collected from this sample in air (red spectrum in Figure S6b). This detected SFG signal was a combination of signals from the prism/nanostructure interface and the oil/air interface. If the roughness/scattering plays a role in reducing SFG signal from the oil/air surface, the SFG signals from these two samples should be similar, both dominated by the contributions from the nanostructure/substrate interface, but this was not the case. Here, the overall signal intensity in spectrum (b) was almost 5 times as strong as that in spectrum (a). The weak intensity from (a) is because of the attenuated IR beam on the oil/air interface due to the strong absorption by oil when penetrating the thick oil layer to reach the oil/air surface, resulting in negligible SFG signal from the oil/air interface. The strong SFG signal intensity in spectrum (b) indicates that the roughness/scattering does not play a significant role in reducing SFG signal from the SLIPS/air (as well as the SLIPS/water) interface.

In addition, we took a picture of the image of the visible laser beam after penetrating through the silicone-SLIPS sample on a mirror (Figure S7). The visible input beam was not scattered by the SLIPS sample. The input IR beam wavelength is longer than that of the visible input beam, thus should have even less scattering compared to the visible beam. This additional experiment shows that scattering was not induced by the nanostructure roughness, because the wavelengths of the beams are much larger than the roughness.

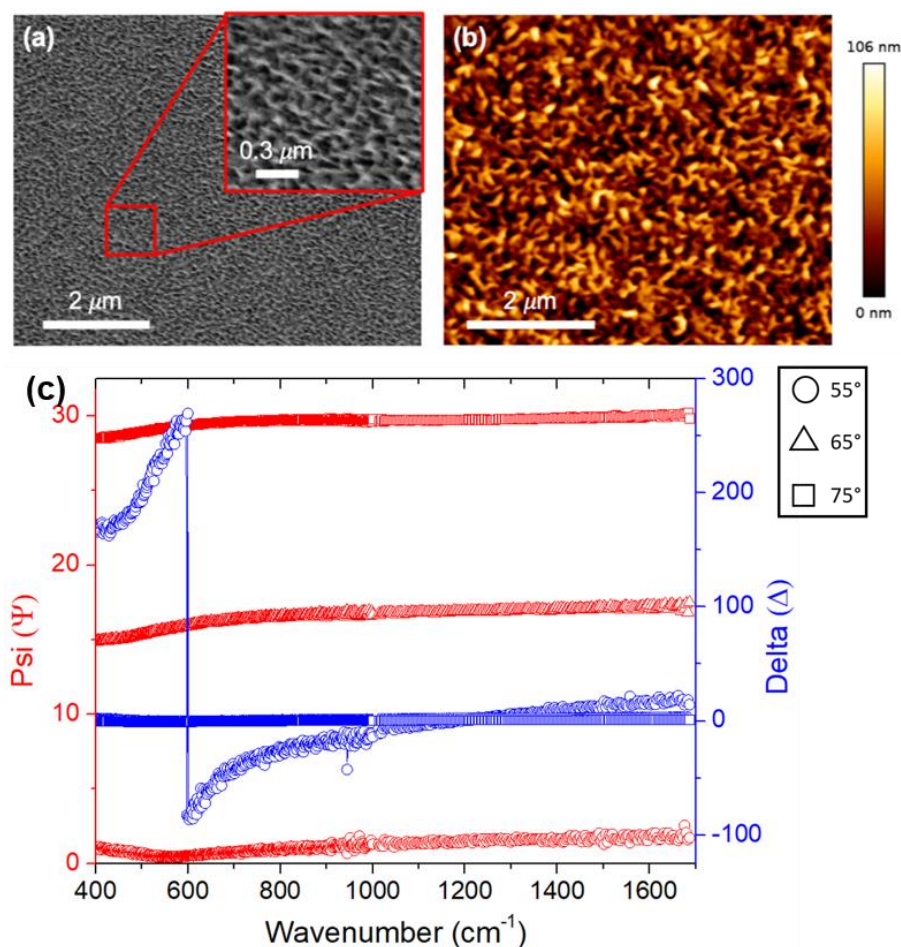


Figure S1. Surface characterization. (a) SEM image of the boehmitized surface. The inset shows a magnified view of the nanoscale roughness. A 5 nm thin-film gold layer was deposited on the boehmitized surface *via* atomic layer deposition to avoid charging during SEM imaging. (b) Atomic force microscopy (AFM) image of the boehmitized surface. The height of the nanoscale features is ~ 100 nm. (c) Ellipsometry characterization of the lubrication oil thickness. Three incident angles (55° , 65° and 75°) were used for data collection. Delta (the phase shift between the two vector components of the elliptically polarized light) and Psi (the amplitude attenuation ratio of the two components) were collected at varying the wavelength of the laser. The data was fitted to obtain the thickness of the lubrication oil.

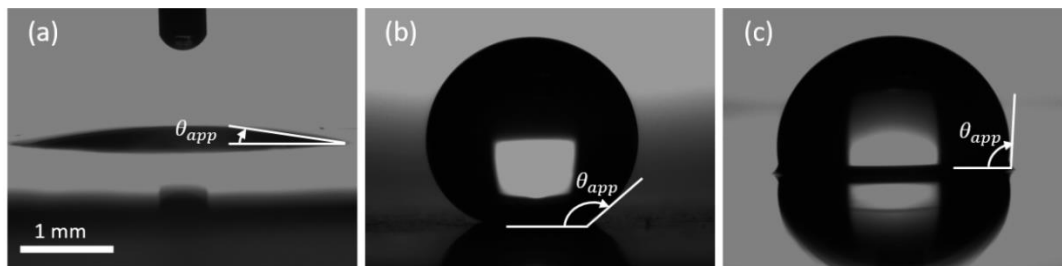


Figure S2. Apparent contact angle. Contact angle of a millimeter size water droplet ($\sim 20 \mu\text{l}$ droplet) on a boehmitized surface (a) before PDMS treatment, (b) after PDMS treatment, and (c) after oil impregnation. Water spreads instantaneously with near zero contact angle on the boehmitized surface. When the boehmitized surface was treated with PDMS, the surface becomes hydrophobic with advancing/receding contact angles of $160^\circ/145^\circ$. When the boehmitized surface was impregnated with oil, the advancing/receding contact angles of a water droplet became $92^\circ/94^\circ$. The standard deviation in the contact angle measurement is $\pm 1-2^\circ$. The same scale bar applies to all figures (a-c).

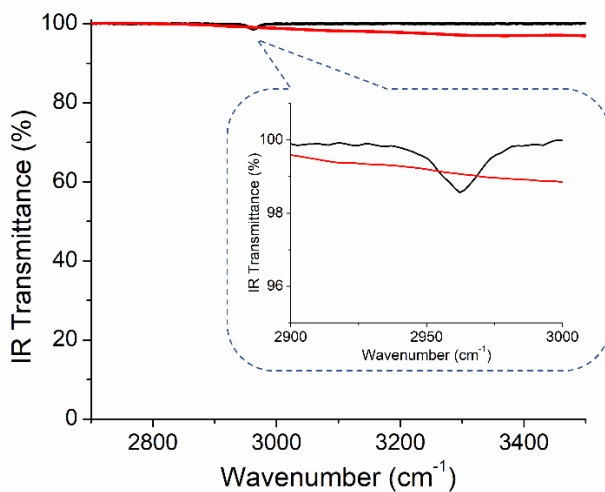


Figure S3. IR transmittance profiles for silicone oil-based SLIPS (black) and fluorinated oil-based SLIPS (red). No substantial absorption was detected for either sample. For both samples, the transmittance was 95-100%, indicating negligible IR absorption by the two (silicone-based and fluorine-based) SLIPS samples.

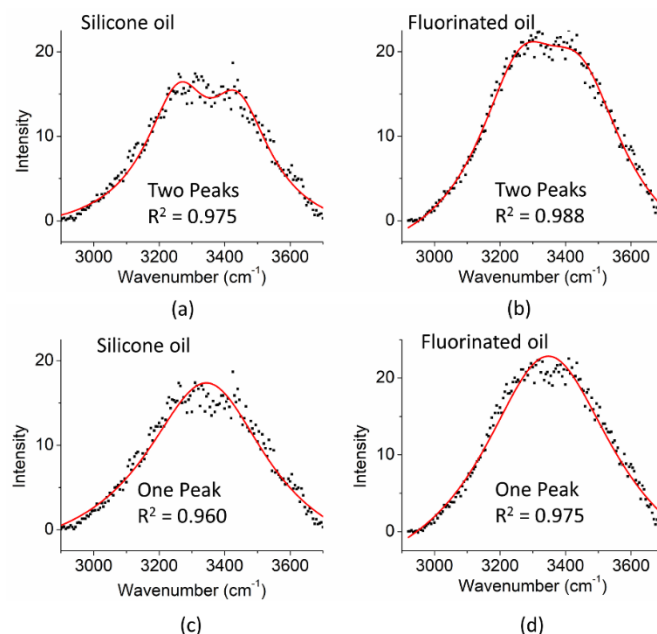


Figure S4. Experimental SFG spectra and fitting results of lubricant oils in contact with isotopically diluted water. Fitting results using two-peak method yielded better results than when one-peak method was used for both silicone oil and fluorinated oil systems, indicating the existence of water molecules in different hydrogen bonding environments.

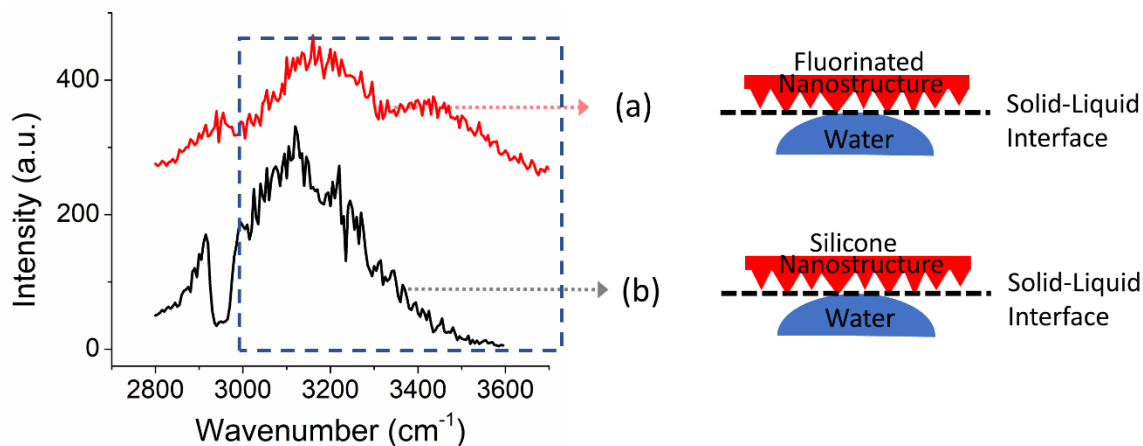


Figure S5. SFG spectra collected from nanostructured substrate/water interface for (a) fluorinated substrate, and (b) silicone substrate, both showing strong water SFG signals. In the absence of lubrication oil, nanostructured substrates alone did not result in disordered interfacial water molecules at the interface, further confirming our hypothesis that beyond immobilizing the lubrication film, nanostructuring offers an avenue to further manipulate interfacial molecular forces.

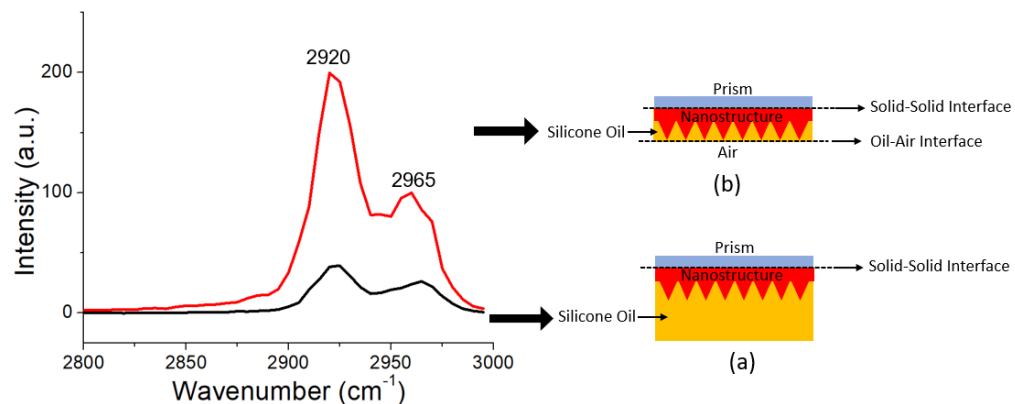


Figure S6. SFG spectra collected from (a) silicone nanostructure in contact with bulk oil layer (black) and (b) silicone SLIPS sample (with a thin oil layer) in air. The much stronger signal detected from (b) demonstrates that the SFG signals presented in this research are indeed generated from the SLIPS/water interfaces, instead of from scattered signals from the nanostructure.



Figure S7. Photographic image of the input visible laser beam after penetrating through the silicone-SLIPS sample collected from a reflective mirror.

Table S1. Physical properties of the lubrication oils used in this study (from the product descriptions from the vendors)

	Silicone Oil 01	Silicone Oil 02	Krytox 100	Krytox 104
Viscosity (cSt)	5 (25 °C)	10 (25 °C)	12.4 (20 °C)	177 (20 °C)
Density (g/mL)	0.913 (25 °C)	0.93 (25 °C)	1.87 (0 °C)	1.93 (0 °C)
Boiling Point (°C)	>140	>140	N/A	N/A
Useful Range ¹ (°C)	N/A	N/A	-70 - 66	-51 - 179

¹From pour point to where evaporation is approximately 10%.

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