Supplementary Information for

Microdroplet Contaminants: When and Why Superamphiphobic Surfaces Are Not Self-Cleaning

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Figures S1 to S16

Other Supplementary Materials for this manuscript includes the following:

Movie M1-8

Description of Movies 1-8:

M1: Water drops on a superamphiphobic surface in the rain (high humidity).

M2: Macroscopic microdroplet spot induced by ethylene glycol.

M3: Macroscopic microdroplet trail induced by ethylene glycol.

M4: Interference microscopy using ethylene glycol.

M5: Interference microscopy using ionic liquid.

M6: < 1 s contact touch by ethylene glycol, leaving microdroplet remnants.

M7: Different liquids on a superamphiphobic surface – drop spots.

M8: Permanent macroscopic microdroplet trail induced by ionic liquid.

Supporting Figures



Figure S1. Representative optical and electron microscopic images of ionic liquid drop trails and spots on soot-templated superamphiphobic surface. a) Drop trails from the use of 30 µL ionic liquid drops that were deposited on soot-templated surfaces before roll-off. Trails were visually discernable particularly after multiple drop roll-offs. b) These imprints are macroscopically large (millimetric due to the drop's original footprint), but are composed of multiple dispersed sub-agglomerate zones that are ca. 1-10 µm in diameters. High magnification scanning electron microscopy images is indicative of the presence of a thin film of liquid that coats the nanoparticles. These agglomerated zones are termed microdroplets or nano-protrusions. c) Drop spots resulting from two ionic liquid drops (30 µL, trihexyltetradecylphosphonium bis(trifluoromethyl sulfonyl) imide (abbreviated bv [P6,6,6,14]⁺[TFSI]⁻)) which were left to sit to the soot-templated surfaces. This was followed by a timely removal after 5 minutes, which left two circular but non-Wenzel-wetted imprints. d) The geometrical nature of agglomerate clusters were identical in both instances.



Figure S2. Supplementary superamphiphobic surfaces (with schematics). a) superamphiphobic but densely packed nanoparticles and b) Superamphiphobic nanofilaments. All particle spheres represented in the schematics should be considered as agglomerates instead of individual nanoparticles.



Figure S3. Interferometric scans (time-ranged) at 633 nm for a drop of ethylene glycol sitting on a superamphiphobic soot-templated surface, focused on the top surface. Time was ranged from 0 s to 330 s. Wavelength: 633 nm. A change of the intensity from bright to dark corresponds to an increase in depth equal to $\lambda/4$, *i.e.* 158 nm.



Figure S4. Plot of surface penetration vs. microdroplet remnants (ethylene glycol on soot). Left axis, mean penetration depth – solid line. Right axis, drop count $(n/\mu m^2)$ - circles.



Figure S5. Universal nature of microdroplet remnants on various superamphiphobic surfaces. Upon drop roll-off after 150 s of a sitting drop, microdroplets were found on a) nanofilaments-based coatings, b) high porosity soot-templated coatings and c) low porosity wet-sprayed coatings. The red background highlights the reflection signal against the less dense and transparent d) nanofilaments, e) porous nanoparticles and f) densely packed nanoparticles respectively. The black regions represent the lack of signal intensity. h-i) Schematics of microdroplet remnants on each surface type. Ethylene glycol was used in this demonstration, highlighted in cyan. All particle spheres represented in the schematics should be considered as agglomerates instead of individual nanoparticles.



Figure S6. Confocal microscopy of a superamphiphobic soot-templated surface, after interaction with a drop of hexadecane. a) A 30 μ L drop of hexadecane (yellow) was left to sit on a soot-templated surface. The hexadecane drop was removed after 5 minutes. After the drop was removed, multiple small microdroplets were observable on the XZ plane. Reflection in red, fluorescently labelled liquid in yellow. b) On the XY plane a "blanket-like" sheet of microdroplets was observed on top of the surface. c) These microdroplets typically disappear under a minute, but can be imaged in 2D down to near-nanometric sizes (0.2-0.7 μ m). Transmission (gray) and fluorescence (yellow) modes were overlaid to enable visualization of the surface.



Figure S7. Confocal microscopy of a superamphiphobic soot-templated surface, after interaction with a drop of undecane. a) A 30 μ L drop of undecane was left on the superamphiphobic surface, which was then removed after 5 minutes. After the drop was removed, a few small microdroplet sites were observable on the XZ plane. b) This was replicated on the XY plane, but no microdroplets were observed even under enhanced gain and constrast. c) It appears that the microdroplets in the systems of undecane are too unstable to be observed in 3D by confocal microscopy. Transmission and fluorescence modes were overlaid to enable visualization of the surface. Color codes are the same as Fig. S6.



Figure S8. XP survey spectra obtained for the neat ionic liquid on a plasma-cleaned silicon wafer (top), the ionic liquid ([P_{6,6,6,14}]⁺[TFSI]⁻, middle), and the pristine soot-templated superamphiphobic surface (bottom). The transitions expected for the ionic liquid (F 2s, P 2p, S 2p, P 2s, S 2s, C 1s, N 1s, O 1s, F 1s, F KLL, and O KLL) are all present. The XP survey spectra obtained for the pristine fluorinated soot surfaces also display the transitions expected (Si 2p, Si 2s, C 1s, O 1s, F 1s, F KLL, and O KLL). The transitions P 2p, S 2p, P 2s, S 2s, and N 1s found for the neat ionic liquid are absent in these spectra. Saliently, the N 1s transition (red dotted square), which is absent in the XP survey spectra obtained for the pristine fluorinated soot surfaces, is found in the survey spectra obtained for the neat ionic liquid in soot trails. This evidences the remaining of ionic liquid on the surface.



Figure S9. Scanning electron microscopy of liquid microdroplets. The presence of liquid microdroplets can grow from a) mild-penetration with thin layers of liquids on the nanoparticle agglomerates, to deeper penetration in b-c) moderate- to severe- penetration and infusion. Liquid appears to permeate agglomerates (highlighted in red), with liquid penetrating at least a few micrometers of the surface. Ionic liquid was used to enable high vacuum analysis of surface features.



Figure S10. Moving fluorescent drop on a fluorinated glass slide. a) This was conducted by immobilizing the drop using a metal plate while moving the substrate below. Imaging was performed on the XY plane of the substrate surface. Two velocities were used: b-c) 10 μ m/s and 300 μ m/s. In both instances, the drop did not leave traces on the substrate, besides catching on c) a small dust particle found on the surface. As the dust is a surface defect that protrudes out geometrically, it retains lubricant, per mechanisms described.



Figure S11. Scanning electron microscopy on an ionic liquid drop spot imprint on a surface coated with superamphiphobic soot-templated nanoparticles. Border of the drop contact is represented by blue highlighted lines. a) A defective zone found at the edge of the border, which can be used as a point of reference. a, inset, optical photograph. No surface penetration is observed. However, a macroscopic (millimetric) and b-d) microscopic morphology variation is evident within these domains. e) A pristine surface is presented alongside for reference. Ionic liquid, trihexyltetradecylphosphonium bis(trifluoromethyl sulfonyl) imide (abbreviated by [P6,6,6,14]+[TFSI]-), was used during this analysis.



Figure S12. Confocal microscopy evaluation of the ionic liquid's vertical contact line advancement into the superamphiphobic layer (typically ranging from 20-35 μ m in heights). a) The macro XZ plane showing the vertical, Z-axial contact line, which impales the superamphiphobic layer over an extended time (5-20 minutes). Surface impalment is represented as a percentage of the total height of the superamphiphobic layer. The fluorescently labeled liquid appears in purple reflections from the liquid-air and the glass-air interfaces in red. b) Representative images (XY plane) showing a "roll-off" cycle of bulk ionic liquid, leaving microscopic remnants in the fluorescent channel as purple. c) A top down view of the 3D scan (XYZ) of the resulting surface, with fluorescently labeled ionic liquid microdroplets scattered across the interface. Notably, the microdroplets do not penetrate the surface, but instead remain largely on the surface at > 70 % of the film height. Images with (in gray) and without the transmission mode are presented to highlight the orientation of the microdroplets within the film. d) A single XZ plane capturing a few distinct droplets that constitute the macroscopic trail/spot is presented.



Figure S13. Increasing surface impalement of soot-templated superamphiphobic surfaces. Two other transitory states exist: a) Partial and b) complete infiltration of the interfaces by ionic liquid, resulting in larger and thicker liquid-on-structure clusters, which ranges from 10 μ m to above. In some instances, SAs can increase to 25-40° within contaminated zones. c) Optical shadowgraphy of sliding drops ([P_{6,6,6,14}]+[TFSI]- (one frame before motion) within pristine vs. significantly penetrated spot and trail domains. Distinctive drop deformation was observed in the latter despite macroscopically clean drop removal. d-e) Contact and roll-off angles of drops within pristine and altered interfaces, showcasing elevated roll-off angles due to pinning.



Time

Figure S14. Microdroplet clusters: Mechanism and Morphology. a) Pristine soot-templated superamphiphobic surfaces are hierarchical, highlighted by sharp peaks across the surface. A briefly deposited drop (< 5 minutes) appears to collapse the surface into a more compact configuration before pinching off a newly configured lump. This leads to the formation of already-impaled zones, which remain even after drop removal. b) Representative schematic of a). All particle spheres represented in the schematics should be considered as agglomerates instead of individual nanoparticles.



Figure S15. Test liquids used for demonstrating drop spots on a soot-templated surface. a) Water, ethylene glycol, ionic liquid and hexadecane drops (30 μ L). Left on surfaces for approximately 5 mins before removal. b) Distinctive spots formed under the ethylene glycol and ionic liquid drops (partial Wenzel-wetting for the ionic liquid system), while nothing was macroscopically observed for the water and hexadecane drops.



Figure S16. Compression of a ionic liquid probe droplet by the AFM tip on the chosen sample. a) Geometrical profiles will include a load, F; a drop height component, h; a top radius contact, r; 2 contact angles, θ_0^A and θ^A , on the probe and the sample respectively. The actual contact radius R can be estimated from this profile, modified with $\theta_0^A < 90^\circ$. b) The actual dimensions of the ionic liquid drop (base 46 µm, height 13.3 µm – represented upside down) was used during our computational estimates.