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Achieving a slippery, liquid-infused porous surface with anti-icing properties by direct deposition of flame synthesized aerosol nanoparticles on a thermally fragile substrate

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Slippery, liquid-infused porous surfaces offer a promising route for producing omniphobic and anti-icing surfaces. Typically, these surfaces are made as a coating with expensive and time consuming assembly methods or with fluorinated films and oils. We report on a route for producing liquid-infused surfaces, which utilizes a liquid precursor fed oxygen-hydrogen flame to produce titania nanoparticles deposited directly on a low-density polyethylene film. This porous nanocoating, with thickness of several hundreds of nanometers, is then filled with silicone oil. The produced surfaces are shown to exhibit excellent anti-icing properties, with an ice adhesion strength of ~ 12 kPa, which is an order of magnitude improvement when compared to the plain polyethylene film. The surface was also capable of maintaining this property even after cyclic icing testing. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4981905>]

Slippery, liquid-infused porous surfaces (SLIPs) are nature inspired surfaces that are designed to repel liquid and solid materials.¹ These surfaces have been shown to pose anti-icing properties,² which broadens the available end-uses from the chemical industry to arctic transportation and energy production. The method behind repellency of SLIPs relies on preventing outside liquids from penetrating the surface structure to the Wenzel state. Instead, the slippery liquid within the porous solid supports the Cassie-Baxter state (instead of air, here the porous structure is filled with lubricant), where the reduced area of the porous solid surface is available to interact with the liquid or ice to be repelled.³ The difference between Wenzel and Cassie-Baxter states is illustrated in Figure 1. This phenomenon is exploited in many superhydrophobic surfaces where an air cushion is entrapped within the porous solid surface. As a result, spherical water drops easily roll off the surface (and have static contact angles larger than 150° ⁴).

The porous structure can be achieved, for example, with nanoposts or with a fibrous material, such as the PTFE-fibre film. We propose an alternative route for producing a SLIPs via direct nanoparticle surface coating utilizing Liquid Flame Spray (LFS^{5,6}) LFS is a promising method as it enables *in-situ* processing and is more readily scalable on various substrate materials than other methods, both chemical and mechanical,⁷ and is more cost efficient than most approaches reported in the literature to process porous surfaces.

The preparation of the SLIPs samples in this work consists of two distinct phases: first, coating of a substrate with

titania (TiO_2) nanoparticles and second, infusing the porous layer with oil. This process is schematically illustrated in Figure 2.

A $20\ \mu\text{m}$ thick low-density polyethylene (LDPE) film was used as the substrate for the SLIPs. This material was chosen for its wide spread use and inexpensiveness. Also, LDPE being thin and thermally fragile, it can be easily substituted with more robust materials like metals and glasses. The required porous layer was achieved by coating the substrate with titanium-oxide agglomerates with $20\text{--}30\ \text{nm}$ primary particle size. The nanoparticle synthesis was carried out with LFS by introducing a $12\ \text{ml/min}$ liquid precursor feed of titanium(IV) isopropoxide (TTIP, Alfa Aesar, 97+) and isopropyl alcohol (VWR, HPLC grade), with a titanium mass concentration of $50\ \text{mg/ml}$, into a turbulent oxygen-hydrogen flame ($\text{H}_2/\text{O}_2 = 50/15\ \text{lpm}$). The substrate was passed through the flame ($15\ \text{cm}$ from the base of the burner), with a velocity of $50\ \text{m/min}$, 10 times.⁵ This repeated coating process produces a $0.5\text{--}1\ \mu\text{m}$ thick coating

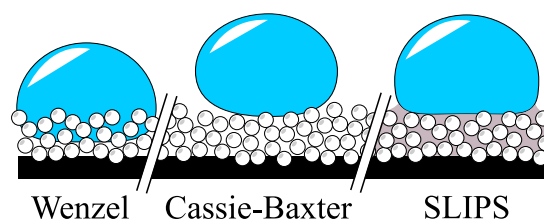


FIG. 1. The manifestation of Wenzel and Cassie-Baxter states on a surface coated with nanoparticles. In SLIPs, the Cassie-Baxter state is favored due to oil filled pores.

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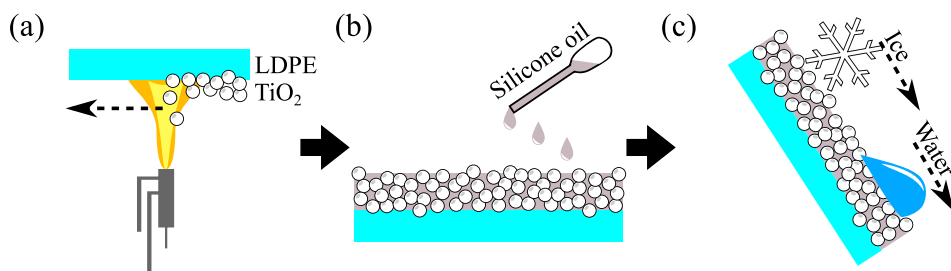


FIG. 2. Schematic illustration of the preparation of SLIPS. Sub-figures depict: (a) nanoparticle synthesis with LFS and subsequent deposition on LDPE, (b) filling the porous structure with oil, and (c) the final surface exhibiting icephobicity and water repellency.

with excess of 90% porosity.⁸ This porous structure was then pipetted full with silicone oil with a viscosity of 50 cSt (25 °C, Sigma Aldrich). A great deal of care was taken not to overfill the samples with the oil, by letting the oil infiltrate into the structure on its own, as not to only test the oil surface in the following tests.⁹ For reference purposes, additional surfaces were prepared with only a porous non-oiled nanoparticle coating and a plain LDPE film surface with added silicone oil.

The surfaces were tested with a contact angle meter (KSV Instruments CAM 200) to characterize the static water contact (WCA) and dynamic sliding (WSA) angles. The WCA and WSA testing was carried out with automatic dispensing of 5 and 10 μl water droplets, respectively. The sliding angles were measured in the range of 0 to $\sim 90^\circ$, and if no sliding was observed, the droplet was deemed pinned to the surface.

Next, icing behavior was evaluated by accreting ice on the surface in an icing wind tunnel located in a cold climate room.¹⁰ The temperature was kept at -10°C , and the air flow velocity was set to 25 m/s. The mixed ice was accreted from supercooled water droplets, with a volume median diameter of 31 μm . Ice adhesion strength values were measured through centrifugal force required to detach the ice from the surface. The sample, with accumulated ice of mass m and contact surface area of A , is attached to a radial arm of length r that spins with a constant angular acceleration α (300 rpm/s), which

yields a following ice adhesion strength via shear stress at detachment time t .

$$\tau = \frac{F}{A} = \frac{mr\omega^2}{A} = \frac{mr(\alpha t)^2}{A}. \quad (1)$$

This cycle of water behavior testing followed by the ice adhesion strength testing was carried out for four times followed by final WCA and WSA measurements.

Furthermore, the produced nanocoating was imaged using a field-emission scanning electron microscope (FESEM, Zeiss ULTRaplus) to ascertain the uniformity of the coating and verify the primary particle size of the agglomerates. SEM micrographs of the surface are shown in Figure 3.

Measurements were performed for three different surfaces: LFS treated, which consists of TiO₂ nanoparticle coated LDPE, oiled plain LDPE, and the complete SLIPS, which has both TiO₂ nanostructures and oil. For reference purposes, also commercially available PTFE-tape was tested in the ice adhesion strength measurements.

The WCA measurements indicate that the apparent contact angles between the water droplet and both oiled surfaces are similar. However, to balance the interfacial tensions between the solid and the liquids, oil forms an annular wetting ridge around the water droplet (Figure 1), preventing us from seeing the real water-solid contact angles, which are higher than the apparent ones.^{11,12} These results are shown in Figure 4. The superhydrophobicity of the initial TiO₂ surface is also clear with its WCA value being over 150° . The WCA values decrease as the titania nanocoating is stressed over the cyclic buildup and removal of ice, which can be

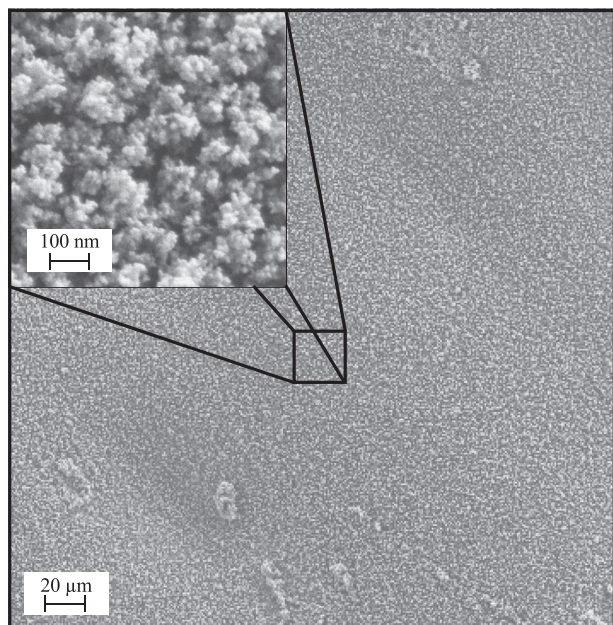


FIG. 3. FESEM micrographs of LFS coated LDPE. The layer has not been infused with oil here.

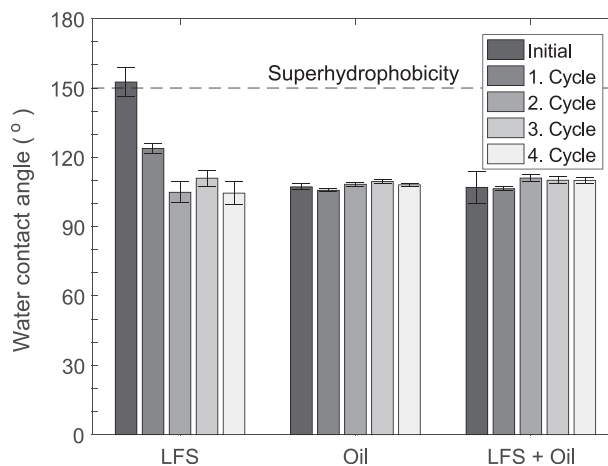


FIG. 4. Apparent water contact angle measurements before and after each of the four ice adhesion tests. The inset shows the superhydrophobicity of the initial LFS coating. Error bars denote standard deviation between four parallel measurements.

caused by the pressure and shear forces affecting the structure or the coating losing its surface hydrocarbons.¹³

The WSA measurements show that even though the nanocoating is initially superhydrophobic based on its contact angle, the droplets are pinned to the surface, which can be tilted upside down without losing the droplet from the surface. This is explained by water's ability to penetrate into the porous structure (the droplet resides partially in the Wenzel state).¹⁴ The initial surface of the oil-infused structure displays a complete opposite behavior with a water sliding angle value of $\sim 3^\circ$, which satisfies the additional requirement for superhydrophobicity of WSA lower than 10° . This value shows an increase in the level of the plain oiled surface after the first cycle of the ice adhesion testing. The results of these measurements are given in Figure 5. The change in the WSA after the first testing cycle indicates a change in the surface caused by the icing and de-icing process. Either the surface roughness is reduced, which has been shown to affect wetting properties,¹⁵ or the oil coverage is affected over the topmost peaks of the porous nanoparticle structure.

The ice adhesion measurements reveal a significant difference in the anti-icing capabilities of the oil-infused surface when compared to a surface without oil impregnation. As can be seen in Figure 6, the nanoporous coating is capable of holding the oil at the solid-ice interface and thus reducing the ice adhesion. The SLIPS exhibits values averaging at 12 kPa, which has improved by almost a factor of three compared to the plain oiled LDPE film surfaces averaging at 34 kPa. Comparably, the non-oiled nanoparticle coating alone cannot replicate the results either. As is highly probable based on the WSA measurements, water droplets get pinned to the surface, and thus, the ice will have a mechanical hold on the surface, resulting in mechanical interlocking effect¹⁶ and an increased ice adhesion strength. All of the oiled samples were also notably better icephobic surfaces than the reference PTFE-tape (WCA = 110° , WSA = 10°), which can be clearly seen in the lowest ice adhesion strength values of the PTFE-tape and the SLIPS, 44 and 9 kPa, respectively.

The results from the cyclic ice adhesion testing show excellent performance, which can be attributed to the ideal

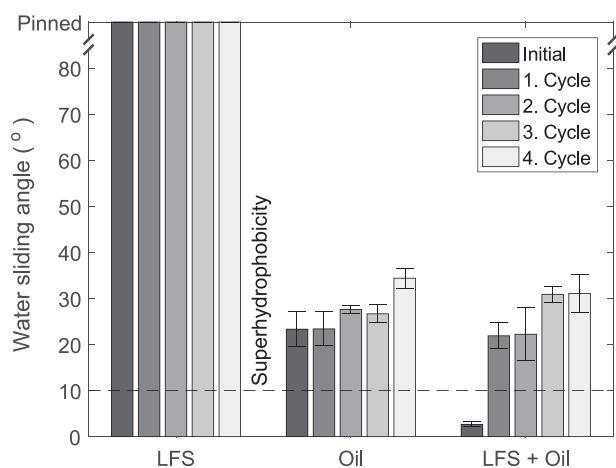


FIG. 5. Water sliding angle measurements before and after each of the four ice adhesion tests. Insets show the pinning of the water droplet on the initial LFS coating and the sliding angle on silicone oil coated smooth LDPE ($\sim 25^\circ$). Error bars denote standard deviation between four parallel measurements.

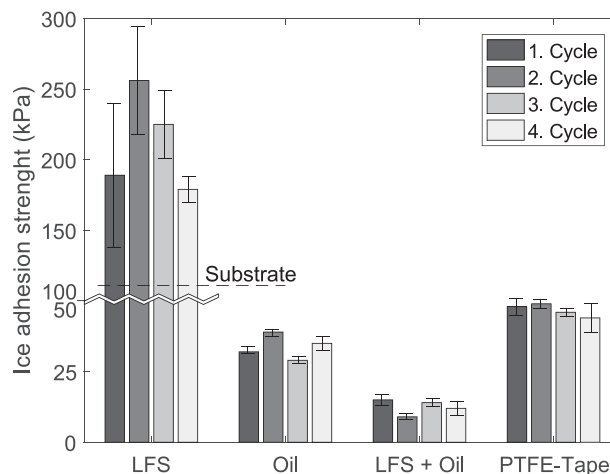


FIG. 6. Ice adhesion measurement results. Ice adhesion strength of the plain LDPE surface is 110 kPa. Error bars denote standard deviation between four independent measurements.

testing of new samples. For further study, these samples should be tested cyclically or in climate conditions until some form of aging can be observed, e.g., due to lubricant loss in dynamic water-air-lubricant interfaces¹⁷ or restructuring of the nanoparticle layer.¹³

Slippery, liquid-infused porous surfaces were prepared by introducing silicone oil into porous TiO_2 nanoparticle coating, generated with flame based aerosol synthesis method, LFS. These surfaces were shown to exhibit excellent anti-icing properties in cyclic ice adhesion testing. The substrate material of LDPE was transformed into SLIPS, and in the process, its ice adhesion strength decreased an order of magnitude from 110 kPa to 12 kPa, which lasted for several testing cycles. Furthermore, after performing the process on a thermally fragile material, it can be performed on other materials with better confidence. These results were also obtained without the typically used fluorinated compounds and with a scalable method.

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