Ultrafast Processing of Hierarchical Nanotexture for a Transparent Superamphiphobic Coating with Extremely Low Roll-Off Angle and High Impalement Pressure

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Low roll-off angle, high impalement pressure, and mechanical robustness are key requirements for super-liquid-repellent surfaces to realize their potential in applications ranging from gas exchange membranes to protective and self-cleaning materials. Achieving these properties is still a challenge with superamphiphobic surfaces, which can repel both water and low-surface-tension liquids. In addition, fabrication procedures of superamphiphobic surfaces are typically slow and expensive. Here, by making use of liquid flame spray, a silicon dioxide–titanium dioxide nanostructured coating is fabricated at a high velocity up to 0.8 m s\(^{-1}\). After fluorosilanization, the coating is superamphiphobic with excellent transparency and an extremely low roll-off angle; 10 µL drops of n-hexadecane roll off the surface at inclination angles even below 1°. Falling drops bounce off when impacting from a height of 50 cm, demonstrating the high impalement pressure of the coating. The extraordinary properties are due to a pronounced hierarchical nanotexture of the coating.

Superamphiphobic surfaces are characterized by their low adhesion to both polar and nonpolar, low-surface-tension liquids.\(^{[1-5]}\) Drops deposited on such surfaces adapt a spherical shape with a static contact angle larger than 150°. More importantly, when moving the contact line, the apparent receding contact angle\(^{[6]}\) exceeds \(\approx 140°\). As a result, drops can roll off the surface at low inclination angles, typically below 10°. The early approaches to design superamphiphobic surfaces were reported by Tsuji et al.\(^{[3]}\) in 1997 and Tuteja et al.\(^{[2]}\) in 2007. After this, superamphiphobic surfaces have been in spotlight of research both from the fundamental and economical aspects. Full comprehension of the super liquid-repellency mechanisms is a prerequisite to realize the potential of superamphiphobic surfaces in applications ranging from protective and self-cleaning materials\(^{[4,7]}\) to medical devices\(^{[8,9]}\) and gas exchange membranes.\(^{[10]}\)

Spray methods are potential candidates for scaled up fabrication of super liquid-repellent surfaces.\(^{[15,16]}\) Particularly, liquid flame spray (LFS) has been applied to produce superhydrophobic surfaces in high-speed roll-to-roll processes.\(^{[17-19]}\) In LFS, a liquid feedstock is injected and atomized in an oxygen-hydrogen flame. Dissolved in the liquid are organometallic precursor molecules. After evaporating and reacting in the flame they form nanoparticles. These nanoparticles are collected on the surface. With the heat from the flame the particles partially sinter together to form a stable, highly porous film. Advantages of LFS are that the deposition process is solvent-free and takes only fractions of seconds as the sample is rapidly moved.
through the flame spray even at the velocities of the order of m s\(^{-1}\). In addition, a broad range of materials including vulnerable biomaterials, such as cellulose-based paper and wood can be coated.\(^{[16,20]}\) A certain minimal velocity is required to avoid destroying the substrate.

Here we use LFS to fabricate a superamphiphobic and optically transparent silicon dioxide (SiO\(_2\))–titanium dioxide (TiO\(_2\)) nanoparticle coating on glass. Our coating shows minimal solid–liquid interactions for both high- and low-surface-tension, polar and nonpolar liquids. Drops of water and \(n\)-hexadecane (10 \(\mu\)L) deposited on the surface easily roll off the coating at inclination angles <1\(^\circ\). To our knowledge, this is the lowest roll-off angle toward hexadecane ever reported. To achieve these superior properties, first, we adjusted the surface morphology by varying the ratio of silicon dioxide and titanium dioxide in the coating. Second, after achieving the right morphology, we applied chemical vapor deposition (CVD) of a 1H,1H,2H,2H-perfluorooctyl-trichlorosilane (97% pure, Sigma-Aldrich) to lower the surface energy. In this way, we left the nanoporop morphology of the coating intact. This is necessary to achieve the superamphiphobic properties—already a 20 nm thick additional layer on top of the nanoparticles hinders liquid repellency.

To synthesize the surfaces by LFS, we use hydrogen (50 L min\(^{-1}\)) and oxygen (15 L min\(^{-1}\)) as combustion gases to achieve a turbulent, high temperature flame (\(>2500\) °C),\(^{[19]}\) and inject the liquid feedstock, tetraethyl orthosilicate (TEOS, 98% pure, Alfa Aesar) and titanium(IV) isopropanoxide (TTIP, 97% pure, Alfa Aesar) dissolved in isopropanol (technical grade, Neste), into the flame through a custom-made spray torch at a feed rate of 12 mL min\(^{-1}\) (the overall Si+Ti atomic concentration in the precursor solution was kept constant at 50 mg mL\(^{-1}\)).

Figure 1. The organometallic precursors react and nucleate in the flame to form nanosized oxide particles. The particles aggregate and are deposited directly on the surface—driven by diffusion and thermophoresis through a boundary layer of air at the substrate\(^{[19]}\)—to form a porous coating. More details of LFS method are given elsewhere.\(^{[17–19]}\) Silicon dioxide and titanium dioxide were selected as coating materials since they are widely used in different coating applications such as painting,\(^{[21]}\) cast-,\(^{[22]}\) dip-,\(^{[23]}\) spray-,\(^{[18]}\) and vapor-phase\(^{[4]}\) deposition. Titanium dioxide is well-known for its photocatalytic activity. This property can be utilized in self-cleaning coatings\(^{[24]}\) and to decompose atmospheric pollutants such as nitrogen oxides (NO\(_x\)).\(^{[21]}\)

We first investigate potential of a pure silicon dioxide coating (Si/Ti ratio = 100/0 wt% in the precursor) to form the overhang morphology. From now on, we call this “Si 100 wt% coating.” The coating was synthesized on a smooth glass substrate by injecting TEOS diluted in isopropanol into the upward pointing LFS flame, through which the sample was moved at a velocity of 0.8 m s\(^{-1}\) at the distance of 6 cm from the burner face. Scanning electron microscopy shows that the resulting coating is \(\approx\)100 nm thick and is composed of highly sintered, round sub-micrometer scale clusters evenly distributed on the surface (Figure 1a,g). After fluorination the surface shows moderate liquid repellency with apparent static contact angles of 138° for water (surface tension \(\gamma = 72.8\) mN m\(^{-1}\)), 118° for ethylene glycol (\(\gamma = 47.3\) mN m\(^{-1}\), 99.8% pure, Sigma-Aldrich), and 83° for \(n\)-hexadecane (\(\gamma = 27.5\) mN m\(^{-1}\), 99% pure, Sigma-Aldrich).

To enhance liquid repellency, we use two approaches (Figure 1). First, we substitute part of the silicon dioxide by titanium dioxide in the coating by adding TTIP to the precursor solution (Figure 1, leftmost column). Second, we increase the thickness of the coating by applying 5 LFS coating cycles prior to fluorination (Figure 1, middle column). To gain insight on the individual agglomerate morphology, we collected particles from LFS on transmission electron microscopy grids (Figure 1, rightmost column).

Already 1 wt% addition of titanium atoms with respect to silicon atoms in the precursor (Si/Ti ratio = 99/1 wt%) drastically changes the morphology of the coating. We call this “Si 99 wt% coating.” Figure 1c,h. An energy dispersive X ray spectroscopy (EDS/EDX) analysis indicates that the Si/Ti ratio within the coating is 96.2/3.8 wt% (Figure S1 and Table S1, Supporting Information). The changes become more prominent when the titanium content was increased up to 99 wt% (Si/Ti ratio = 1/99 wt%). We call this “Si 1 wt% coating,” Figure 1e,i. Silicon dioxide is no longer aggregated in highly sintered, dense clusters. Instead, the coating shows increasing amount of porous, nanosized particle aggregates with overhang structures. EDS/EDX analysis shows that the Si/Ti ratio within the coating is 2.1/97.9 wt%. Titanium dioxide exists mainly as anatase with small fraction, 10–15%, of rutile independently on the Si/Ti ratio. Anatase is known to be photocatalytically more active than rutile.\(^{[25]}\) Silicon dioxide remains amorphous.\(^{[18]}\) We speculate that these morphological changes are caused by an early nucleation of titanium dioxide in the cooling flame, while silicon dioxide remains still in vapor phase.\(^{[18,19]}\) Titanium dioxide particles thus act as nucleation sites for silicon dioxide and facilitate formation of the porous particle aggregates within the coating. Silicon dioxide, which sinters at lower temperature than titanium dioxide, acts as a “binding agent” within the coating and thus enhances its mechanical stability (see discussion with drop impact and sand abrasion experiments).

Then we increase the coating thickness by moving the samples through the flame spray 5 sequential times at intervals of \(\approx\)2 s. The growth mechanism of the coating through the boundary layer of air at the surface—driven by thermophoresis and diffusion—induces accumulative growth of large particle aggregates at the surface (Figure S2, Supporting Information). As a consequence, the height of the surface protrusions and hierarchical roughness of the coating increase (Figure 1b,d,f; and Figures S3 and S4, Supporting Information). The final height of the surface textures depends on the coating composition. With highly sintered, dense Si 100 wt% coating the highest protrusions reach \(\approx\)700 nm after 5 coating cycles (Figure S3, Supporting Information). With Si 1 wt% coating the highest peaks of the surface texture are \(\approx\)700 nm already after the first coating cycle (Figure 1j) and reach a height of at least 7 \(\mu\)m after 5 cycles (Figure 1k; and Figure S4, Supporting Information).

After a single LFS coating cycle, referred to as “thin coating,” the best liquid repellency is given by Si 1 wt% coating. Water drops deposited on the surface adapt a spherical shape with static contact angle >160°. 10 \(\mu\)L sized drops roll off the surface as soon as the substrate is inclined by less than \(\approx\)3°. With ethylene glycol and \(n\)-hexadecane, the static contact angles
approach 150° but the drops pin to the surface, i.e., roll-off angles are typically >10° (Table 1).

A coating with superamphiphobic properties was achieved by coupling the two approaches, i.e., by reducing the amount of Si/Ti ratio in the precursor from 100/0 wt% to 1/99 wt% and by increasing the number of coating cycles from 1 to 5, referred to as “thick coating.” In this way, we obtained a roll-off angle below 1° for 10 µL n-hexadecane drops. Advancing and receding contact angles were 165° with nonmeasurable contact angle hysteresis when the drop volume was increased and decreased between 15 and 25 µL at the rate of 1 µL s⁻¹ using a standard contact angle goniometer (Figure S5 and Video S1, Supporting Information).

The superamphiphobic coating developed here shows extremely low interaction with water and even with n-hexadecane. To our knowledge, the lowest roll-off angles reported for n-hexadecane on superamphiphobic surfaces are 2°–5° depending on the surface and the drop size.[2–5,7,9,10,16] Here, 10 µL drops of n-hexadecane typically rolled off the surface as soon as the goniometer needle tip was detached although the substrate was adjusted in horizontal plane without any apparent inclination angle (Video S2, Supporting Information).
Table 1. Wettability of the liquid-repellent coatings. Apparent static contact angles (CA) and roll-off angles (RA) of 10 μL drops of water, ethylene glycol, and n-hexadecane on coatings with different silicon dioxide content and thickness after chemical vapor deposition of the fluorosilane. “Thin” refers to a single LFS coating cycle. “Thick” refers to 5 subsequent LFS coating cycles. The standard deviations are given by individual contact angle goniometer measurements. Note that contact angles larger than ~155° cannot reliably be measured using the goniometer technique and thus the real error is larger.

| Coating | Water CA/RA [°] | Ethylene glycol CA/RA [°] | n-Hexadecane CA/RA [°] |
|---------|-----------------|--------------------------|------------------------|
| Si 100 wt%, thin | 138 ± 3/1 | 118 ± 1/1 | 83 ± 1/1 |
| Si 100 wt%, thick | 168 ± 1/1 | 154 ± 3/50 ± 3 | 146 ± 1/1 |
| Si 99 wt%, thin | 157 ± 4/13 ± 10 | 126 ± 5/1 | 91 ± 4/1 |
| Si 99 wt%, thick | 168 ± 1/1 | 160 ± 5/6 ± 1 | 153 ± 2/1 |
| Si 1 wt%, thin | 163 ± 2/3 ± 1 | 154 ± 2/12 ± 1 | 151 ± 2/29 ± 7 |
| Si 1 wt%, thick | 167 ± 1/1 | 164 ± 1/1 | 157 ± 4/1 ± 1 |

Our coating consists of random, overhang nanostructures where the diameter of spherical primary particles is ~10–20 nm. We investigated the effect of texture size on water repellency by growing an additional 20 nm thick silicon dioxide layer on the surface using a gas-phase Stöber-like reaction. After growing the silicon dioxide layer (Figure S6, Supporting Information) and modifying the surface with the fluorosilane, the antewetting performance declined. For all coating compositions (Si 100 wt%, Si 99 wt%, and Si 1 wt%) the water contact angle decreased and the roll-off angle increased due to the increased solid–liquid contact area and smoothed out overhangs as compared to the pristine coatings (Table S2, Supporting Information). This underlines the role of nanostructured texture in reducing the solid–liquid interactions on the coating. Coupling this nanostructured texture with pronounced hierarchical surface roughness supports the air cushion below low-surface-tension liquids, however, the liquid still wets large surface area and therefore pins to the solid (Supporting discussion, Supporting Information). To reduce the overall wetted area of the solid and thus adhesion of drops, hierarchical roughness needs to be introduced (Figure 2c). Indeed, several surfaces with inherent hierarchical roughness such as paper,[9] wood,[16] and fabrics[7] serve as ideal substrates for randomly structured superamphiphobic coatings where both polar and nonpolar liquid drops can bead up and easily roll off the surface.

To achieve superamphiphobicity, a nanoscopic overhanging structure needs to be combined with roughness on the >1 μm length scale; in the following we call this a hierarchical structure. Such hierarchical structures need a certain minimum coating thickness. Below this minimum thickness, it might not be possible to create a superamphiphobic surface. The overall solid–liquid contact area would become too large.

Figure 2. Schematic illustration of wetting of a model surface by water and a nonpolar liquid. The surface consists of spherical particles. Penetration depth δ of the liquid around a single particle with radius r depends on the intrinsic wettability of the material, characterized by the Young contact angle θ. a) Water (large θ) wets small fraction of individual particles within the first particle layer, indicated by the dashed line in (b). A nonpolar liquid (small θ) wets large fraction of individual particles and b) invades from one particle to the other into the texture of the solid until θ is reached at the overhangs. c) Hierarchical roughness of the surface has critically important role in reducing the overall solid–liquid contact area and pinning of low-surface-tension liquids on randomly structured superamphiphobic surfaces.
This condition poses a lower limit to the thickness of a superamphiphobic coating on a smooth substrate such as plain glass. Here the coating was not superamphiphobic after one coating cycle when its thickness was \( \approx 700 \) nm (Figure 1j). However, after 5 coating cycles the coating became superamphiphobic (Figure 1k; and Figure S4, Supporting Information). It is reasonable to assume that with most of the randomly structured superamphiphobic surfaces, the hierarchical surface structure increases with increasing coating thickness. For example, the candle soot templated coating remains superamphiphobic only when the coating is thicker than \( \approx 2 \) \( \mu \)m.\[^{[4,26]} \]

We verify optical transparency of our coatings by ultraviolet–visible light transmittance spectroscopy. All thin coatings (coated 1 time) transmit more than 98% as compared to the transmittance through the pristine glass substrate (for wavelengths higher than 500 nm, Figure S7, Supporting Information). Thick coatings (coated 5 times) transmit 97% of the light for Si 100 wt% coating and 79% for Si 1 wt% coating (Figure 3a). High transmittance of light at the visible light spectrum results in good optical transparency (Figure 3b) of the super liquid-repellent coatings (Figure 3c).

In addition to liquid repellency and optical transparency, the impalement resistance of the coating decides about potential applications. How stable is the Cassie–Baxter state before the whole surface texture is wetted by the liquid and the system goes to the so-called Wenzel state?\[^{[27]} \] We investigate the impalement resistance of our superamphiphobic coating by letting water drops impact the surface from different heights. Water drops of 15 \( \mu \)L volume (radius \( R = 1.5 \) mm) were released from heights of 1–200 cm leading to impact velocities \( v \) between 0.4 and 5.4 m s\(^{-1}\). This approaches the terminal velocity of falling medium-sized rain drops (\( R < 1 \) mm).\[^{[28]} \] Such an impact velocity and drop radius corresponds to Weber numbers up to \( We = \rho v^2 R / \gamma = 600 \). Here, \( \rho \) is the density of water = 1 g cm\(^{-3}\). The drops always rebounded from the surface and no impalement was observed.

To prevent full or partial penetration of the impinging drops,\[^{[31]} \] the capillary pressure \( P_C \) generated within the textures should be higher than the maximal effective hammer pressure \( P_E \), which is the upper limit for the pressure the surface can experience during the impact. For drops impacting on horizontal flat surface, one can estimate the maximal hammer pressure\[^{[29]} \]

\[
P_E = 0.2 p C v
\]

Here, \( C \) is the sound velocity (for water \( C = 1497 \) m s\(^{-1}\)). For an impact velocity \( v = 5.4 \) m s\(^{-1}\) and water the hammer pressure can be estimated to be 1.6 MPa. The maximal capillary pressure developed within the particle-like surface texture to prevent the impalement can be estimated from\[^{[30]} \]

\[
P_C = \frac{2 \gamma a}{d} \sin \theta_{adv}
\]

Here, \( d \) is the mean distance between protrusions, \( r \) is the radius of the constituting particles, and \( \theta_{adv} = 119^\circ \) is the advancing contact angle of water on a smooth fluorosilane coated silicon oxide. When the hammer pressure \( P_E \) exceeds \( P_C \), one expects the Cassie–Baxter state to collapse. With roughly \( r = 5–10 \) nm and setting \( P_E = P_C \) we get a required maximal spacing of protrusions = 18–26 nm. On our coating, the smallest pores between the particles and their aggregates can fulfill this criterion (Figure 1f,i). It is expected that the liquid will penetrate in between the largest protrusions on the surface. These protrusions dampen the impact and relief the pressure experienced by the surface in between them. For comparison, on a rectangular array of the fluorosilane modified SU8 micro-pillars with solid area fraction of 0.06 (5 \( \mu \)m side wall, 10 \( \mu \)m height, 15 \( \mu \)m spacing, fabricated by photolithography\[^{[31]} \]) impalement of impacting 15 \( \mu \)L water drops occurred already at the hammer pressure of \( \approx 240 \) kPa (release height = 3 cm, impact \( v = 0.8 \) m s\(^{-1}\), \( We = 12 \)).

The superamphiphobic coating also repels impalement of impacting \( n \)-hexadecane drops (\( R = 1 \) mm, \( p = 0.773 \) g cm\(^{-3}\)).\[^{[32]} \]

Figure 4. At 1 cm release height the 5 \( \mu \)L drop bounced 4 times before settling down at the surface (\( v = 0.4 \) m s\(^{-1}\), \( We = 5.4 \), Video S3, Supporting Information). At 10 cm release height the drop bounced 6 times before settling down (\( v = 1.4 \) m s\(^{-1}\), \( We = 55 \), Video S4, Supporting Information). The \( n \)-hexadecane drops even rebound when released from a height of 50 cm. The corresponding impact velocity for the drop was 3 m s\(^{-1}\) (\( We = 250 \)). Above the release height of 50 cm, the kinetic energy becomes large as compared to the surface tension causing that the rim of the drop breaks up and many satellite drops are generated. Because of the breakdown of the drop, at higher release heights it becomes difficult to reliably determine whether the drop partially impales the coating. Calculating the pressure experienced by the surface during impact of the \( n \)-hexadecane drop with Equation (1) and a speed of sound
in \(n\)-hexadecane = 1339 m s\(^{-1}\)) we get \(P_e = 650\) kPa for the impact from the height of 50 cm. Assuming that this pressure is balanced by the capillary pressure (Equation (2)) a protrusion spacing of maximal \(d = 13–18\) nm is allowed when \(\theta_{adv} = 77^\circ\) is the advancing contact angle of \(n\)-hexadecane on a smooth fluorosilane coated silicon oxide. This is in the same order of magnitude that we got for the maximal spacing with water.

The mechanical stability of the superamphiphobic coating (Table S3, Supporting Information) was tested by letting 15 \(\mu\)L water drops impact on the surface from the release height of 200 cm at \(v = 5.4\) m s\(^{-1}\). The sample was tilted by 10\(^\circ\) to ensure rapid removal of the impinging drops. The coating could withstand at least 20 000 drop impacts (90 impacts min\(^{-1}\)) by completely allowing the impinging drops to bounce off the surface. After the experiment, roll-off angle of 10 \(\mu\)L water drops at the impacted area was 13\(^\circ\). The nanotexture was partially damaged and \(n\)-hexadecane drops started to pin to the impacted surface (Figure S8, Supporting Information). With increasing silicon dioxide content the mechanical stability of the coating increased against impacting drops. After 20 000 drop impacts on both the Si 100 wt% and Si 99 wt% coating the roll-off angle of 10 \(\mu\)L water drops remained at 3\(^\circ\)–5\(^\circ\). That is, the surfaces remained superhydrophobic after the exposure to the impacting drops.

To further test the robustness of the superamphiphobic coating (Si 1 wt%, coated 5 times), in particular the adhesion of the coating to the glass substrate, we exposed the surface to steam and continuous water flush. Therefore, water was heated in a beaker on a hot plate at 150 °C and the sample was placed face down 5 cm above the water surface for 1 h. In a second set of experiments, the surface was rinsed with Milli-Q water flow at \(v = 1.7\) m s\(^{-1}\) for 1 h. After both treatments, the roll-off angle for 10 \(\mu\)L water drops remained unchanged, i.e., <1\(^\circ\), which indicates good adhesion of the coating. Additionally, the adhesion of the coating was tested by adhering and peeling off an adhesive tape (Scotch Magic), applied with the pressure \(2.5\) kN m\(^{-2}\) for 60 s. After the tape test, the coating maintained a low roll-off angle for both water and \(n\)-hexadecane, <1\(^\circ\) and 6\(^\circ\) ± 2\(^\circ\), respectively.

Abrasion by impacting sand particles can locally damage the superamphiphobic coating (Si 1 wt%, coated 5 times). After impacting the surface with 100–200 \(\mu\)m diameter sand grains from the height of 2 cm for 10 s (5 g of sand; impact \(v = 0.63\) m s\(^{-1}\); sample was adjusted at an angle of 45\(^\circ\)), \(n\)-hexadecane drops pinned to the surface. However, water drops kept the high static contact angle = 155\(^\circ\) and roll-off angle = 25\(^\circ\) after the abrasion. Although the impact of the sand particles damaged the top part of the protrusions, the measurements indicate that the adhesion of the coating to the glass substrate was not compromised, i.e., it exceeded the cohesive strength of the coating. Si 100 wt% coating (coated 5 times) remained superhydrophobic after the sand abrasion test and maintained a low roll-off angle = 2\(^\circ\) for 10 \(\mu\)L water drops.

Temperature-stability of the superamphiphobic coating (Si 1 wt%, coated 5 times) was investigated between −200 °C and +500 °C. Delamination of the coating was not observed even after freezing the sample in liquid nitrogen for ≈30 s (Figure S9, Supporting Information). Roll-off angles for water and \(n\)-hexadecane remained <1\(^\circ\) and 10\(^\circ\) ± 5\(^\circ\), respectively. Heating the sample in an oven at 500 °C for 3 h degraded the

**Figure 4.** 5 \(\mu\)L \(n\)-hexadecane drops (\(R = 1\) mm) impinging the superamphiphobic surface at different velocities. The snapshot images of a high-speed camera (2000 fps) show the maximum spreading and takeoff of the drops within the first and the second rebound at the surface at a) impingement velocity \(v = 0.4\) m s\(^{-1}\) (release height = 1 cm, \(W_e = 5.4\)) and b) \(v = 1.4\) m s\(^{-1}\) (release height = 10 cm, \(W_e = 55\)). At the higher impingement velocity \(v = 1.4\) m s\(^{-1}\) the drop generated a satellite drop within the impact, which is merging with the main drop after the second rebound.
fluorosilane layer. After reapplying the fluorosilane, the coating recovered its high static contact angle >160° and low roll-off angle <1° for both water and n-hexadecane.

Photosensitivity of the superamphiphobic coating (Si 1 wt%, coated 5 times) was investigated by illuminating the surface with UV-A light (2.3 ± 0.3 mW cm⁻²) up to 4 h. After 40 min of illumination, 10 µL drops of n-hexadecane pinned to the surface (Table S4, Supporting Information) because of photodegradation of the fluorosilane coating on top. To delay this, before the fluorination we encapsulated the coating with a ∼3 nm thick silicon dioxide shell by applying a gas-phase Stöber-like reaction for 4 h. Such a thin passivation layer did not reduce the superamphiphobic properties of the coating. Moreover, the coating remained superamphiphobic even after the UV-A illumination of 4 h: roll-off angles for 10 µL water, and n-hexadecane drops were <1° and 4°±2°, respectively.

Robustness of the air cushion on the superamphiphobic coating (Si 1 wt%, coated 5 times) under prolonged contact with n-hexadecane was investigated by letting 10 µL drops to rest on the surface for 30 min. The static contact angle remained unchanged within the experimental error (Figure S10, Supporting Information). After the period of 30 min, roll-off angle for the n-hexadecane drops was 10°±2°, proving the stability of the air cushion.

In summary, we introduce an up-scalable method to fabricate optically transparent superamphiphobic surfaces with low drop adhesion and high impalement resistance against both high- and low-surface-tension liquids. With LFS and by mixing Si and Ti precursors, surfaces can be fabricated with high apparent contact angles and low roll-off angles below ≈1° even for n-hexadecane. To achieve an ultralow drop adhesion for nonpolar liquids, the superamphiphobic surface needs to fulfill the following criteria: (1) low-surface-energy chemistry, (2) nanoscale, overhang surface structures, (3) hierarchical roughness, and (4) sub-micrometer scale pore size to increase the critical impalement pressure. We show that increasing the Ti content or increasing the number of coating cycles increases porosity, thickness, and hierarchical structure of the coating. Both measures improve the superamphiphobic properties. On the other hand, optical transparency of the coating decreases and better mechanical stability is achieved with a high Si content. The Si/Ti ratio needs to be optimized depending on the specific requirements for the coating.

Experimental Section

Surface Modification: Prior to CVD with the fluorosilane the samples were activated by oxygen plasma (Femto low-pressure plasma system, Diener electronic, Germany) at 300 W for 10 min. The samples were placed in a desiccator together with 100 µL of the fluorosilane and the pressure was reduced to ∼200 mbar for 2 h. After the CVD, the samples were placed in a vacuum oven at 60 °C for 2 h to remove unreacted silane. To investigate the effect of the size of surface textures on the wetting properties of the coatings, a gas-phase Stöber-like reaction was applied for selected samples (Si 100 wt%, Si 99 wt%, Si 1 wt%, coated 1 time). The samples were placed in a desiccator together with ammonia (3 mL) and TEOS (3 mL) at atmospheric pressure and room temperature for 24 h. This resulted in growth of an additional 20 nm thick porous silicon dioxide shell around the particles.[39] After the silicon dioxide growth, the samples were sintered in an oven at 500 °C for 3 h and subsequently fluorinated by the CVD process. Sintering induces compaction of the silica shell. To delay photocatalytic degradation of the fluorosilane, the superamphiphobic coating (Si 1 wt%, coated 5 times) was passivated by growing a thin, ∼3 nm thick silicon dioxide layer on the surface by applying the gas-phase Stöber-like reaction for 4 h. After this, the coating was fluorinated by CVD. The coating was not sintered in the oven.

Microscopy/Spectroscopy: For SEM imaging (LEO 1530 Gemini, Zeiss), the samples were sputter-coated with a nm thick Pt layer to reduce the surface charging. The used sputtering time would yield a layer thickness of ∼7 nm on a smooth substrate. TEM imaging was performed with a JEM-2010 instrument. The samples were collected on lacy carbon film on copper grid (Agar) directly from LFS at the distance of 6 cm from the burner face by moving the grid through the flame at the velocity of 0.8 m s⁻¹. The chemical composition of the coatings was investigated using a Hitachi SU8000 SEM equipped with EDS/EDX. For the analysis, the porous oxide coatings (coated 5 times) were scraped from the glass substrate onto a conductive carbon tape to exclude any Si signal originating from the substrate. At least 3 measurements at different positions were conducted. An inverted laser scanning confocal microscope (Leica TCS SP8 SMD, Leica Microsystems) with HC PL APO CS2 40×/1.10 water objective was used to capture a micrograph of a water drop resting on Si 100 wt% surface.

Wetting Properties: Static contact angles with 5 µL drops and roll-off angles with 10 µL drops of water, ethylene glycol, and n-hexadecane were measured by DataPhysics OCA 35 goniometer (DataPhysics Instruments) using 3–5 individual measurements at different positions on each sample. Static contact angles larger than 155° cannot reliably be measured using the goniometer technique as for high contact angles real position of the base line is difficult to determine and even small variation greatly influences the measured values. Although the measured values may be too low, the trend should be correct. Advancing and receding contact angles were measured by increasing the drop volume from 0 to 25 µL and decreasing the volume back to ∼0 µL at the rate of 1 µL s⁻¹. The dynamic contact angles were carefully analyzed using Fiji,[33] an open-source image processing software. Contact angle hysteresis was determined using drop volumes of 15–25 µL to prevent that the goniometer needle affected the results.[34] Impingement dynamics of 5 µL n-hexadecane drops were investigated using Photron Fastcam Mini UX100 high-speed camera (2000 fps).

Illumination and Light Transmittance: To test UV stability, the samples were illuminated by UV-A light (intensity = 2.3 ± 0.3 mW cm⁻²) from the distance of 8 cm (light source: LQ-400, Dr. Gröbel UV-Elektronik GmbH). Intensity of the illumination was measured using an UV-radiometer RM-12 with UV-A sensor for spectral range of 315–400 nm (Dr. Gröbel UV-Elektronik GmbH). Ultraviolet-visible light spectrometer (Lambda 25, PerkinElmer) was used to investigate light transmittance of the coatings.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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