Simple Fabrication of Robust Water-Repellent Surfaces with Low Contact-Angle Hysteresis Based on Impregnation

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In the past decades, extensive research efforts have been carried out to create water-repellent surfaces. Inspired by nature,[1–3] combinations of physical and chemical modifications of a surface can be employed to enhance the water repellency (hydrophobicity).[4,5] The ability of such surfaces to mimic the functions of the natural hydrophobic surfaces finds widespread applications in various fields. Commonly employed approaches to increase the hydrophobicity are based on the modification of either physical or chemical properties of a surface. For example, in the case of physical patterning of a hydrophobic material, the surface roughness can be considerably increased to reduce the surface-liquid contact area by introducing air pockets within the structure.[6–8] In this case the wetting behavior can be controlled by tailoring the surface topography, and ideally a superhydrophobic surface is obtained. Superhydrophobic surfaces are usually characterized by specifying the static contact angle (CA) and contact angle hysteresis. One disadvantage of such surfaces is that heterogeneous wetting (Cassie-Baxter regime) can turn into homogenous wetting (Wenzel regime) by external stimuli such as pressure, vibration or electric fields.[9–13] The Wenzel regime is usually characterized by strong pinning which stands in conflict with the desired water repellency. Essentially, it is the CA hysteresis rather than the CA that determines the water repellency of a surface.

In the past few years, a lot of research has been conducted towards creating surfaces with low CA hysteresis. In that context it needs to be taken into account that CA hysteresis may have different origins. On the one hand, the roughness of the surface, which causes "physical" pinning of the 3-phase contact line, should be small (physical homogeneity). Additionally, the chemical composition of the surface material has to be homogenous (chemical homogeneity). Furthermore, adsorption and desorption of molecules between the liquid and the surface should be avoided, otherwise it would lead to energy dissipation during the droplet motion and result in higher hysteresis.[14,15] This mechanism may be the cause for the contact angle hysteresis observed even on atomically smooth surfaces.[16–18]

Coating a substrate with low surface energy materials is one possibility to reduce the heterogeneities and to create surfaces with low hysteresis. Although the number of different coating methods reported in the literature is continuously increasing, the most common method still is to synthesize a monolayer on the surface by using silane/siloxane related chemistry.[19–21] However, manufacturing such surfaces requires a certain background and experience in chemistry. Krumpfer et al.[22,23] demonstrated a less involved method by using simple silicone chemistry, creating a monolayer on a silicon wafer by immersing it into polydimethylsiloxane, resulting in a relatively small CA hysteresis.

Recently, a completely different approach has been employed to achieve liquid repellent properties using structured surfaces impregnated with a lubricating film.[24–28] As an example, a Teflon membrane acts as a matrix for perfluorinated liquid, resulting in a surface from which various liquids roll off easily. In this case the common gas-liquid-solid wetting state is replaced by a gas-liquid-liquid wetting state. However, the necessity of a fluorinated (ensuring complete wetting) and relatively thick matrix, required for retaining the supporting film, may impede a technological implementation. Additionally, using fluorinated chemicals may interfere with environmental protection requirements.[29]

Another possibility to implement a similar approach for water-repellent surfaces is based on silicone oil acting as a lubricating film. For that purpose a suitable matrix has to be developed to keep the film on the surface. Liu et al.[29] used an organogel-based matrix, which they synthesized on various substrate materials. This requires time consuming steps (summing to more than one day) and a comparatively complex chemistry.

Here, we present a very simple and fast method of manufacturing water-repellent surfaces on several materials based on impregnation with silicone oil (**Figure 1**). For preparing the sample a substrate is covered with a thin silicone-oil film annealed for 2–3 min at 300 °C. Heating of the substrate leads to the formation of a thin silicone layer on the surface, after which it is impregnated with silicone oil. That way, the surface becomes water-repellent, with a contact angle hysteresis below 4° on various substrate materials. The preparation of the surface takes only about 5 minutes, while the impregnated substrates are stable over a long time period, even when stored with the surface-normal perpendicular to the gravitational field. Finally, we present a possible application of such surfaces in microfluidics, using thermocapillarity to transport small water droplets.

As mentioned above, the fabrication method presented here (Figure 1) is very simple and can be used for various substrate materials. For coating the different substrates mostly silicone oil of low viscosity (5 cSt) was used. Low viscosity allows for

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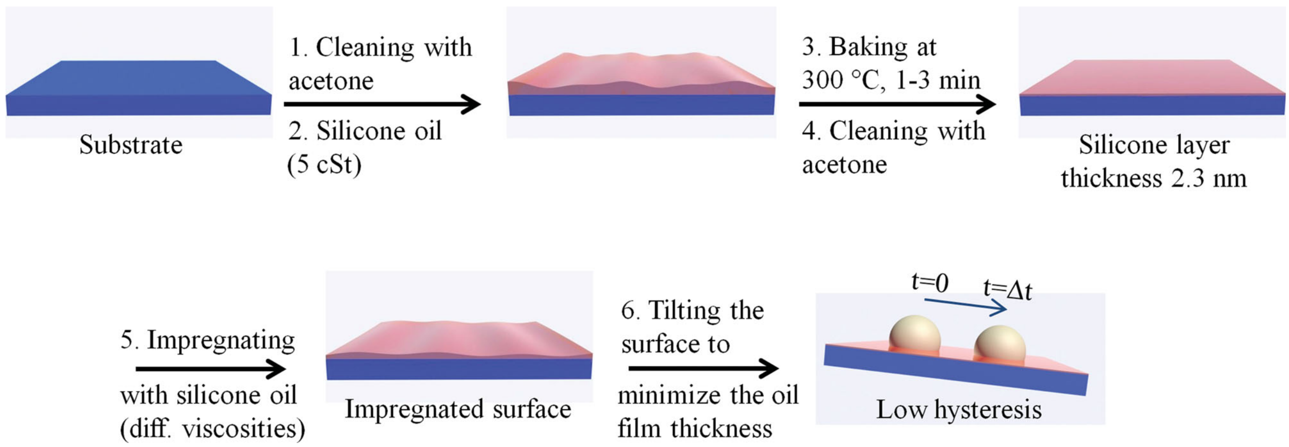

Figure 1. Schematic showing the preparation of a water-repellent low-hysteresis surface based on impregnation with silicone oil.

faster spreading on the substrate which leads to a rapid formation of a thin oil film. Additionally, during the annealing process the film thickness changes significantly due to thermocapillary motion. Silicone oil exhibits a decreasing surface tension with increasing temperature. Exposed to a temperature gradient, thermocapillary shear stresses build up, resulting in a film flow towards the cooler side of the substrate. Because of the inhomogeneous temperature distribution on most hot plates, this flow was always observed and helps speeding up the coating process compared to a situation with uniform temperature. However, we did not observe a complete dewetting, which confirms the results reported in the literature.[30] During annealing a part of the oil film evaporated leaving a solid layer on the substrate. The thickness of the solid layer was determined by ellipsometry to be about ≈200 nm. After cleaning the surface with acetone the layer thickness was reduced to 2.3 nm. XPS results (not shown) indicate that the distribution of chemical elements in the thin layer is identical to that of silicone oil. AFM and SEM measurements show that the silicone oil residue is flat and homogeneous, see Figure S1 (supporting information). After the layer was formed, a liquid silicone film was applied onto the substrate to form an impregnated surface. **Table** 1 shows advancing and receding contact angles as well as the contact angle hysteresis of a water droplet, both before and after the final impregnation step. The samples without lubrication film (cleaned with acetone) showed significantly higher CA hysteresis compared to the impregnated surface. We also observed that the CA of unimpregnated substrates depends on the annealing temperature if the latter is below 150 °C, which was already discussed by Krumpfer et al.[23] By contrast, for temperatures between 150 and 300 °C no significant temperature dependence of the CA was found on glass substrates. However, we observed some slight non-reproducible fluctuation of the CA hysteresis, which vanished after impregnation.

After impregnation the hysteresis decreased considerably achieving values below 4°. The advancing contact angle varied between 102° and 107°, depending on the substrate material. We suppose that the silicone layer obtained via annealing serves two different purposes. Firstly, it prevents contact between the water droplet and the surface material, which reduces pinning because of the chemical homogeneity of the layer. Secondly, the layer helps keeping the lubrication film on the surface. The residual silicone layer seems to enhance the affinity of the surface to the applied oil film. This is confirmed by experiments on silicone oil spreading, which was faster on annealed substrates compared to untreated ones. Using ellipsometry and interferometry we determined the oil thickness after surface preparation to be approximately 2.7 µm. To investigate the stability of the film we used impregnated stainless steel and aluminum foils. After the samples were prepared they were fixed on a vertical holder tilted by 80–90° with respect to the direction of gravity. Two weeks later, the CA hysteresis was measured again, giving no indications of significant changes with respect

Table 1. Advancing contact angle θ_A, receding contact angle θ_R and related contact angle hysteresis θ_H of water on various substrates before and after impregnation. All samples were annealed at 300 °C using silicone oil (5 cSt). The same oil was used as lubrication film.

	Before impregnation			After impregnation		
Materials	θ_A	θ_R	$\approx \theta_H$	θ_A	θ_R	$\approx \theta_H$
Stainless Steel	107.5 ± 1.9	83.0 ± 2.7	24.5	104.7 ± 0.6	102.1 ± 1.6	2.6
Glass	106.8 ± 1.8	94.0 ± 5.0	12.7	106.8 ± 2.8	103.9 ± 2.9	2.9
Silicone wafer	107.1 ± 2.8	87.1 ± 6.4	20.0	104.4 ± 1.9	102.0 ± 2.3	2.4
Aluminum	104.9 ± 3.7	76.9 ± 6.3	28.0	106.8 ± 2.5	104.9 ± 1.4	1.9
Brass	107.2 ± 3.7	82.7 ± 13.2	24.5	104.7 ± 1.5	102.9 ± 2.8	1.7
Copper	105.5 ± 2.0	83.4 ± 2.2	22.1	102.7 ± 1.2	98.8 ± 3.8	3.9

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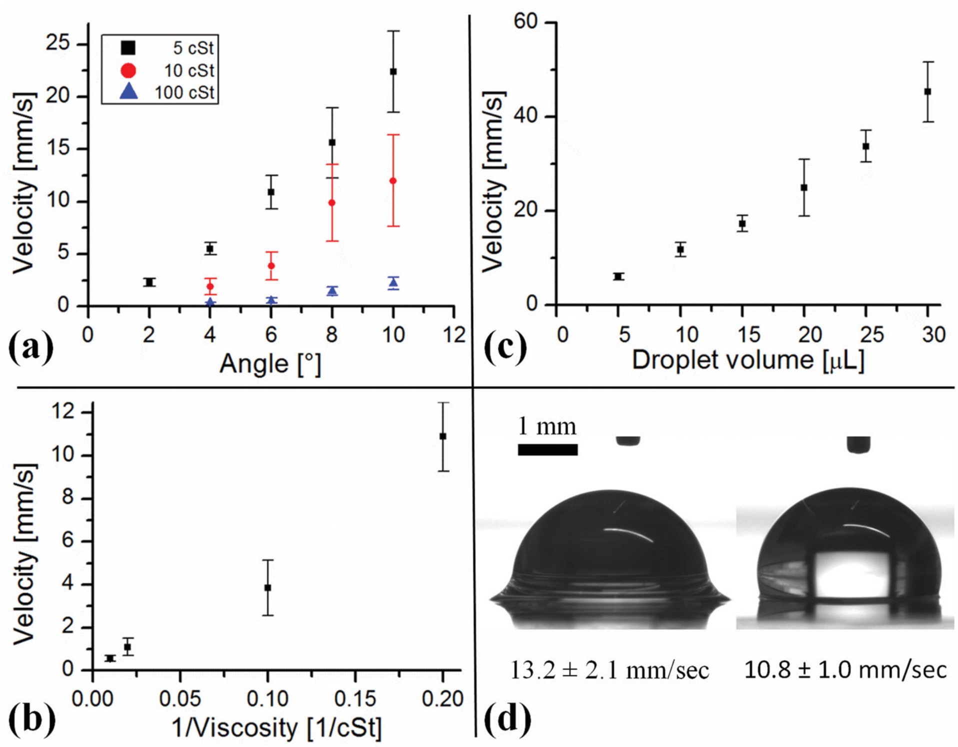

Figure 2. a) Dependence of the velocity of a 10 µL water droplet on the inclination angle for lubricating films with different viscosities. b) Velocity of a 10 µL droplet at an inclination angle of 6° on impregnated substrates with different film viscosities. c) Droplet velocity at an inclination angle of 6° for different droplet volumes. d) Droplet morphologies for a thick (left) and thin (right) lubrication film. All samples were prepared on a glass substrate.

to the original measurements. The observed reduction of the film thickness after several hours in tilted position seems to be due to evaporation and not due to gravitation.

The silicone-oil impregnated substrate has the advantage of tunability. By using silicone oils with different viscosities acting as lubricating film the roll-off velocity of a droplet on an inclined surface can be tuned. In **Figure 2**a the dependence of the droplet velocity on the inclination angle is shown for different lubrication film viscosities. Starting from a critical angle the velocity seems to increase approximately linearly with the roll-of-angle and higher viscosities of the lubricating film cause a significant influence resulting in lower velocities. This can be used as a tuning parameter for different applications.

General investigations by Smith et al.[31] about lubricant-impregnated surfaces on nanostructured substrates provide several approximations of how the film viscosity and other parameters influence the droplet velocity. They determined the velocity magnitude by balancing the gravitational force with the viscous dissipation force. The analysis reveals that viscous dissipation in the silicon-oil rim around the droplet (compare Figure 2d left) yields the dominant contribution. According to this model the velocity of the rolling droplet u is inversely proportional to the dynamic viscosity μ of the film $u \propto 1/\mu$. Figure 2b displays this dependence. Within the given error bars, the linear dependence on $1/\mu$ is reproduced.

In Figure 2c the dependence of droplet velocity on its size is presented. As expected, increasing the size of the droplet leads to higher velocities due to the stronger gravitational force.

As mentioned before, the lubrication film appears to be remarkably stable, and dryout of the substrate was not observed even after two weeks in a vertical position. However, the film thickness directly after impregnation is relatively large and can be inferred from images of droplets wetting the substrate (Figure 2d left). It can be seen that close to the droplet the silicone oil surface assumes a rim shape, characteristic for wetting of a liquid film by a second liquid.[32] After tilting the surface the film thickness decreases considerably, which may play a role for the roll-off velocity of droplets. To study the influence of the film thickness, a silicone layer was prepared on a glass substrate and covered with a comparatively large amount of 5 cSt silicone oil (Figure 2d left). The velocity of a 10 µL droplet on the obtained substrate tilted by 6° was measured to be 13.2 ± 2.1 mm/s. Subsequently, the oil film thickness was reduced via tilting the substrate by 90° and keeping it in that position for 15 min. This results in a significantly smaller silicone oil rim around a water droplet (Figure 2d right). With that configuration the velocity measurement was repeated, resulting in a value of 10.8 ± 1.0 mm/s, which shows that in both cases similar velocities are observed. However, in the case of a thick lubrication film one would intuitively expect lower droplet velocities due to the motion through the liquid film. Our experimental results show that is not the case. This observation is in agreement with the model formulated by Smith et al.,[31] where the influence of viscous dissipation within the lubrication film is negligible compared to dissipation in the oil rim, and its roll-off velocity is not influenced by the height of the oil rim around the droplet. We believe that the marginal difference in droplet

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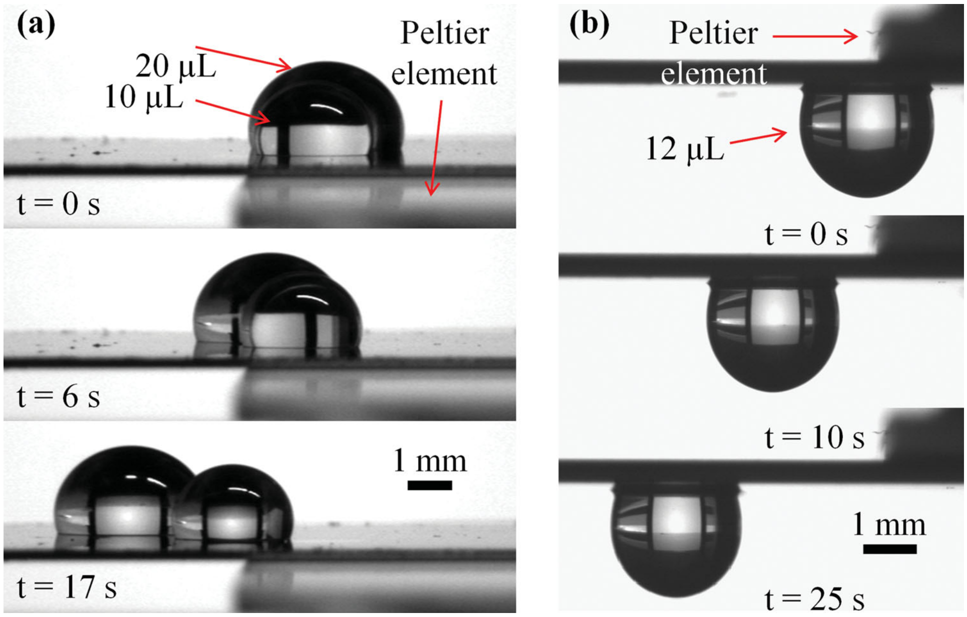

Figure 3. a) Simultaneous thermocapillary motion of 10 and 20 µL droplets. b) Thermocapillary motion of a 12 µL droplet "upside down". In both cases stainless steel was used as substrate material.

velocity on lubricating films of different thickness is mainly due to roughness or contaminations of the surface that may impede the droplet motion on comparatively thin films.

Owing to the fact that silicone-oil based low-hysteresis surfaces are robust and extremely easy to fabricate, a broad spectrum of applications is conceivable. Here we demonstrate the feasibility of droplet transport by temperature gradients, which may find applications in microfluidics as a powerful method to control and manipulate small amounts of liquid. Thermal gradients can be easily formed using microheaters, radiative heating or other sources where energy dissipation occurs.[33] The thermocapillary motion of a liquid drop arises due to variations of interfacial tensions with temperature.

With respect to the situation considered here, it needs to be taken into account that not only the droplet, but also the underlying liquid film can be set into motion by thermocapillary stresses. We observed this behavior by using very thick oil films, comparable to the situation shown in (Figure 2d left). When applying a temperature gradient to the silicone-oil impregnated surface, a water droplet deposited on the surface is set into motion. This raises the question of whether droplet transport occurs through the motion of the lubrication film acting as a "conveyor belt" or through droplet motion relative to the film. To answer this question, a simple experiment was performed. According to Pratap et al.[34] the thermocapillary velocity of a droplet on a solid surface increases proportional to its footprint radius. By contrast, if the motion of the lubrication film is responsible for droplet transport, the velocity should be independent of the droplet size. Therefore, in the experiment the motion of two droplets of different size was compared. For this purpose, a low-hysteresis surface was prepared on a stainless-steel substrate, having a comparatively high thermal conductivity. At one end of the stainless-steel plate a Peltier element was placed, heating the substrate. Two different droplets with volumes of 10 µL and 20 µL were placed on the surface, with centers of mass having nearly the same x-coordinates (the direction of the thermal gradient), while the droplet-to-droplet spacing in y-direction was about 2 mm. The setup was constructed such that the two droplets are exposed to the same thermal gradient. Snapshots of the droplet motion after the Peltier element was switched on are displayed in **Figure 3**a. It is found that the 20 µL droplet moves faster than the 10 µL, arriving at a higher terminal velocity. This indicates that the origin of droplet transport is not the motion of the supporting lubrication film. When studying the thin film alone (without droplets) under the influence of a thermal gradient, no significant film motion or even dewetting of the substrate could be detected which confirms the results found in the literature.[30] This does not stand in contradiction with the observations reported above in context with the annealing process, since the latter films are much thicker.

The thermocapillary motion of droplets on silicone-oil impregnated surfaces benefits from the fact that the CA (about 106°) is significantly smaller than that on superhydrophobic surfaces (CA > 160°), which may also exhibit a very small contact-angle hysteresis. Owing to this fact, the contact surface between the droplet and the substrate is larger than on superhydrophobic surfaces, allowing for larger thermocapillary forces. Because of the larger contact area it is also possible to flip the surface and drive hanging droplets by thermocapillarity. In Figure 3b droplet transport in such an "upside down" mode is shown. Again, a stainless steel substrate locally heated using a Peltier element was used. Such experiments further corroborate the robustness and reproducibility of the wetting properties of silicone-oil impregnated surfaces.

In conclusion we presented a simple fabrication method for low-contact-angle-hysteresis surfaces on various substrates and studied their wetting properties. In all of the studied cases the

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resulting contact-angle hysteresis of water droplets was below 4°. The silicone-oil film impregnating the surface was found to be surprisingly robust. Even after storing a sample for two weeks in a vertical position (tilted by 90° with respect to the gravitational field), the contact-angle hysteresis remained virtually unchanged, and no dryout of the surface was observed. It was shown that by using different lubrication film viscosities, the droplet roll-off velocity on inclined surfaces can be tuned. It was also observed that the thickness of the lubrication film does not influence the droplet velocity, which adds to the robustness of such surfaces. Furthermore, a potential application was demonstrated by studying the thermocapillary motion of water droplets along the surface. It was shown that transport is due to the motion of droplets relative to the lubrication film, rather than due to thermocapillary motion of the film itself. Owing to a relatively small contact angle of about ≈106° (compared to superhydrophobic surfaces) it could by demonstrated that even hanging drops can be transported using temperature gradients.

Experimental Section

Materials: Silicone oils of viscosities 5 cSt, 10 cSt and 50 cSt were obtained from Sigma-Aldrich and of 100 cSt from GM-Racing. Various substrate materials, including silicon wafer, aluminum, brass, stainless steel, glass slides and copper were used.

Surface Preparation Procedure: A schematic of the surface preparation is shown in Figure 1. Before coating, the substrates were cleaned with acetone. Then 10 µL of 5 cSt silicone oil was spread evenly onto the substrate with a pipette, after which the substrate was baked for 60–180 s at 300 °C on a VMS-C7 hot-plate (VWR). Residual oil was removed by rinsing the substrate with acetone. Subsequently, silicone oil was again spread evenly over the surface. To minimize the oil film thickness the substrate was left for 15 min at an angle of approximately 80° – 90° with respect to the direction of gravity.

Surface Characterization: Static, advancing and receding contact angles of 5 µL water droplets on the modified surfaces were measured using a Krüss DSA 100 contact angle instrument. The reported angle values are generally an average over 15 measurements made on 3 separately prepared samples. Ellipsometry measurements were performed with Accurion EP3 imaging ellipsometers. XPS measurements were carried out using a self-designed XPS-system (Phoibos 150, Specs). Interferometry was performed with a 3D optical profiler (PLµ Neox Sensofar).

Droplet velocities on tilted surfaces were determined by placing a substrate on a fixed stage with a defined angular incline. Droplets were deposited onto the substrate and released to roll down under the influence of gravity. Videos of rolling droplets were recorded using the Krüss goniometer system. Pixel-meter calibration was performed by measuring the pixel length of a reference object. Droplet velocities were computed from the recorded videos using the NIS elements AR 3.0 software.

Supporting Information

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

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