Surface Chemistry

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Superoleophobic Coatings with Ultralow Sliding Angles Based on Silicone Nanofilaments**

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Inspired by the self-cleaning and water-repellent properties of the lotus leaf[1] and the leg of the water strider[2] in the natural world, artificial superhydrophobic surfaces have generated extensive attention in academia and industry.[3] It is well-known that combining appropriate surface roughness and materials with a low surface energy is a successful way to prepare superhydrophobic surfaces.[4] However, it is not so easy to create superoleophobic surfaces that resist wetting of nonpolar liquids because of their low surface tension (for example, 27.5 $\mathrm{mN\,m^{-1}}$ for hexadecane and 23.8 $\mathrm{mN\,m^{-1}}$ for decane compared to 72.8 $\mathrm{mN\,m^{-1}}$ for water).

From experience in designing superhydrophobic surfaces, many groups have tried various techniques to create superoleophobic surfaces.[5,6] However, most of the reported superoleophobic surfaces are limited to nonpolar liquids with surface tensions of more than 27 $\mathrm{mN\,m^{-1}}$. Moreover, the droplets often have high contact angles (CA $\approx 150°$) but adhere on the surface and cannot roll off, even when the surface is turned upside down.[6] In fact, it is very challenging to create superoleophobic surfaces on which the droplets of nonpolar liquids could roll off easily (sliding angle (SA) $< 10°$) as the interaction between droplets and surfaces should be very weak.[7] Both a special microstructure and materials with very low surface tension are necessary. Until now, only a few studies have reported such low SA for nonpolar liquids by using inherently textured fabrics as substrates or by introducing some specially designed patterns, such as overhang structures and re-entrant surface curvatures.[8] However, the fabrication of such microstructures is limited to particular substrates (such as silicon wafers and aluminum foil) or relies on complicated etching-in methods (such as lithography and anodization), which means a significant restriction of applications.

Herein, we present a novel simple grow-from approach for the fabrication of superoleophobic surfaces by the combination of versatile organosilanes. Coating of surfaces with organosilanes is well-known because of its fine properties and simplicity.[9] The structure and properties of the coatings are determined by many factors, including the number of organosilane reactive groups, alkyl group structure, and reaction conditions.[10] Thus, there are many chances to tailor properties of the coatings. In 2003, we prepared for the first time a new group of nanostructures called silicone nanofilaments by chemical vapor deposition of organosilanes on various substrates.[11,12] The coatings exhibit excellent superhydrophobicity and chemical and environmental stability.

For the fabrication of superoleophobic coatings herein, silicone nanofilaments with different microstructures were grown in toluene onto glass slides by simply regulating the water concentration during hydrolysis and condensation of trichloromethylsilane (TCMS). Subsequently, the nanofilaments were activated using O_2 plasma and then modified with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (PFDTS; Figure 1). The superoleophobic surfaces thus obtained feature a high CA and ultralow SA for various nonpolar liquids (such as mineral oil, toluene, hexadecane, decane, and cyclohexane), excellent transparency, and chemical and environmental stability.

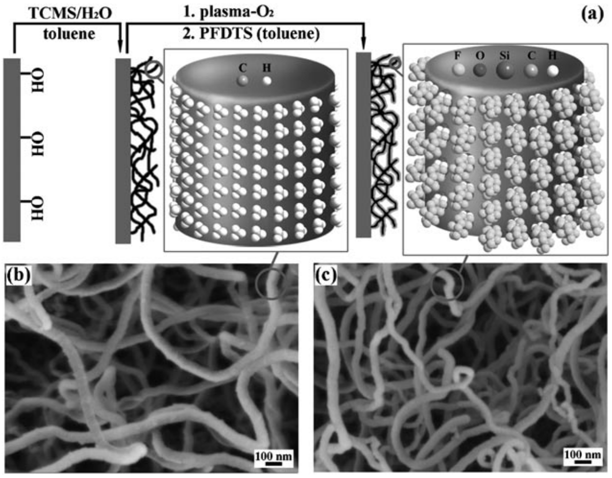

Figure 1. a) Growth of silicone nanofilaments onto glass slides using TCMS and subsequent modification with PFDTS. b,c) Corresponding SEM images of the b) TCMS- and c) TCMS/PFDTS-coated glass slides. Both samples were prepared at $C_{\mathrm{water}} = 124$ ppm.

Once injected into toluene, TCMS will hydrolyze in the presence of water and self-assemble into a crosslinked polymeric network that is composed of a large amount of silicone nanofilaments on the surface of the substrate (Figure 1). The nanofilaments are 50–90 nm in diameter and several micrometers in length, which is somewhat thicker and longer compared to the nanofilaments we previously obtained by chemical vapor deposition.[11] The random growth of the

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silicone nanofilaments generates a rough topography at the surface. The methyl groups at the surface of the nanofilaments decrease the surface tension. A similar conformation of methylene groups of poly(vinyl alcohol) has also been proposed by Feng et al.[13] After TCMS coating, the surfaces became superhydrophobic ($CA_{water} \approx 170°$ and $SA_{water} \approx 3.6°$ depending on the conditions) and superoleophilic ($CA_{hexadecane} \approx 0°$). As the nanofilaments are stable against further modification, they needed to be activated before treatment with PFDTS. Herein, O_2 plasma was applied to convert the hydrophobic methyl groups on the surface of the nanofilaments into hydrophilic hydroxy groups while keeping the silicone skeleton intact. The surfaces became superhydrophilic and superoleophilic. Once the O_2 plasma-treated substrate was immersed in dry toluene that contained PFDTS, the PFDTS molecules preferentially anchored onto the hydroxy groups on the nanofilament surface.

When the glass slides were coated with TCMS at low water concentrations, a high CA and low SA of water were obtained (Supporting Information, Figure S1). With increasing water concentration, a slight decrease of CA and increase of SA were observed. After coating with PFDTS, the surfaces showed a very good superhydrophobicity. The CA and SA of water droplets remained almost constant in the range 56–194 ppm water content during the nanofilament formation (Figure 2). Therefore, the water concentration does not have an observable influence on the wetting properties of the surface when water is used as the probe.

Water droplets are in the Cassie–Baxter state on all of the TCMS- and TCMS/PFDTS-coated glass slides. However, the effect of water concentration is obviously different when hexadecane is used as the probe (Figure 2). Both the CA and SA of hexadecane strongly depend on the water concentration in toluene during TCMS coating. When the water concentration was low (56 and 79 ppm), the hexadecane droplets adhered strongly on the TCMS/PFDTS-coated glass slides even though the CA was about 150°, which indicated that the hexadecane droplets are in the Wenzel state. This phenomenon is frequently observed for most of the previously reported superoleophobic coatings.[6] A significant increase of the CA of hexadecane was observed upon increasing the water concentration to 102 ppm; a further increase of the water concentration to 194 ppm has no significant influence on the CA of hexadecane. A sudden decrease of the SA of hexadecane to about 3° was observed upon increasing the water concentration from 79 ppm to 102 ppm, indicating a transition from the Wenzel state to the Cassie–Baxter state. The SA of hexadecane on all of the TCMS/PFDTS coated glass slides remained below 3° with further increases in water content up to 194 ppm.

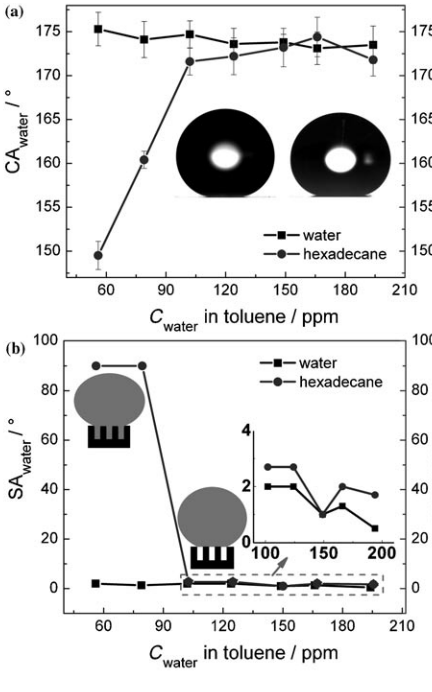

Figure 2. Variation of a) CA and b) SA of water and hexadecane on the TCMS/PFDTS-coated glass slides as a function of water concentration in toluene during the TCMS coating procedure. The inserts in (a) show 5 μL droplets of water (left) and hexadecane (right). The $SA_{hexadecane}$ of 90° in (b) indicates that the droplets were pinned on the surface even when tilted to 90°.

For comparison, a PFDTS-coated glass slide without nanofilaments was also prepared. The CA of water and hexadecane on the sample are 117.7° and 79.6°, respectively; these values are among the highest for self-assembled fluoroalkylsilane films on flat substrates.[14] According to the Wenzel model, the introduction of surface roughness will make the surface more oleophilic if the CA of organic liquids is lower than 90°. Indeed, the surface becomes superoleophobic after nanofilaments are introduced under proper conditions. This observation is similar to the superhydrophobic lotus leaf constructed by surface roughness and a hydrophilic waxy compound.[15]

It has been shown that the described changes of the CA and SA (for both water and hexadecane) are due to the introduction of silicone nanofilaments and different water concentrations during the nanofilament formation. The silicone nanofilaments act as a skeleton for the superoleophobic coatings. It was found that the behavior of the hexadecane droplets on the superoleophobic coatings is closely related to the topography of the skeleton, which can be regulated simply by changing the water concentration in toluene during the TCMS coating procedure (Figure 3; Supporting Information, Figure S2). A dense layer (ca. 600 nm in thickness) of thin and short silicone nanofilaments were grown on the flat glass slide at a water concentration of 56 ppm. With increasing water concentration to 79 ppm, a small amount of long and thick nanofilaments appeared, and an increase of the layer thickness (to ca. 1.5 μm) and surface roughness were observed. The surface topography of nanofilaments obtained under these conditions is sufficient to support the hexadecane droplets in the Wenzel state on the corresponding TCMS/PFDTS coatings. Upon further increasing the water concentration to 102 ppm, a dramatic change of surface morphology was observed. All of the nanofilaments became very thick (ca. 60 nm in diameter; Supporting Information, Figure S3) and long (several micrometers). The nanofilaments loosely stacked together and formed a circa 4 μm thick nanofilament layer, which means an evident increase of surface roughness. Such a surface topography

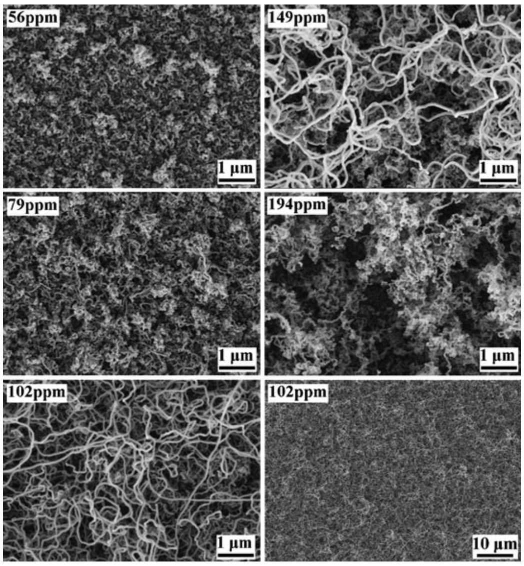

Figure 3. Surface morphology of the TCMS-coated glass slides at different water concentrations in toluene during the TCMS coating procedure. Scale bars: 1 µm, except for the image at the bottom right corner (10 µm).

could trap more air beneath the droplets and successfully alter the hexadecane droplets from the Wenzel state to the Cassie–Baxter state. No obvious changes could be seen upon further increasing the water concentration to 124 ppm except for continuous increase of thickness of the coating (to ca. 6 µm). However, the amount of the thick and long nanofilaments decreased ,and some small nanofilaments beneath them appeared with increasing water concentration to 149 ppm and 166 ppm. Upon increasing the water concentration further to 194 ppm, almost all of the thick and long nanofilaments disappeared and only the small nanofilaments remained, which was responsible for the decrease of thickness of the filament layer to about 4 µm. The small nanofilaments were very similar to those generated at low water concentration, but stacked loosely, which was still sufficient to keep the hexadecane droplets in the Cassie–Baxter state. The very low sliding angle at a water concentration of 194 ppm also indicates that the nanofilaments do not necessarily have to be thick and long; the roughness of the filament layer should be more important in influencing the superoleophobicity. There was no obvious change of surface morphology after modification with PFDTS (Supporting Information, Figure S4).

After confirming the relationship between water concentration in toluene during the TCMS coating procedure, the structure of the coating, and the behavior of hexadecane droplets, the superoleophobicity of the coatings was further tested by recording CA, SA, and kinetic behaviors of various typical liquids with different surface tensions. CAs and SAs of the liquids on the TCMS- and TCMS/PFDTS-coated glass slides are shown in Table 1.

Table 1: CAs and SAs of liquids with different surface tensions on the TCMS- and TCMS/PFDTS-coated glass slides.[a]

	TCMS		TCMS/PFDTS		Surface tension[b]
	CA [°]	SA [°]	CA [°]	SA [°]	[mN m^{-1}]
water	167.8	5.2	173.1	1.3	72.8
diiodomethane	90.9	90	165.7	1.3	50.8
mineral oil	0	–	172.2	1.2	32
toluene	0	–	168.4	2.5	28.4
p-xylene	0	–	171.1	3.0	28.3
n-hexadecane	0	–	174.4	2.0	27.5
n-dodecane	0	–	167.2	2.3	25.4
cyclohexane	0	–	156.6	5.7	25
n-decane	0	–	162.5	5.3	23.8

[a] 5 µL liquid; samples were prepared with C_{water} = 166 ppm. [b] At 20 °C (from reference [16]).

Only water droplets could easily roll off from the surface of the TCMS-coated sample. The CA decreased with decreasing surface tension of the liquid. Liquid droplets with a surface tension of ≤ 32 mN m^{-1} (mineral oil) spread quickly and formed flat liquid films on the TCMS-coated glass slides (for example, mineral oil, toluene, and xylene). For these liquids, the CA was close to zero and no SA could be detected. The TCMS-coated glass slide was totally wetted once dipped in toluene (Supporting Information, Movie S1).

After further modification of the silicone nanofilaments with PFDTS however, the samples showed a different behavior owing to the introduction of fluoroalkyl groups (Figure 4 c). For all of the liquids investigated, even cyclohexane and decane, a high CA (> 155°) and low SA (< 6°) on the TCMS/PFDTS coated glass slides was observed. The liquid droplets could easily roll off from the slightly tilted (3°) TCMS/PFDTS-coated glass slides (Supporting Information, Movie S2). This effect can be attributed to the existence of the air cushion between the solid surface and the liquids,[17] and all of the liquid droplets are in the Cassie–Baxter state. Even jets of toluene and decane could bounce off the TCMS/PFDTS

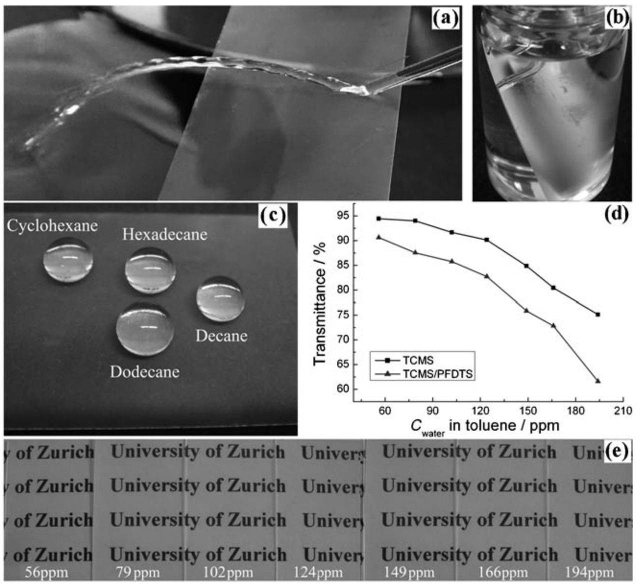

Figure 4. Images of the TCMS/PFDTS-coated glass slides a) with a jet of toluene bouncing off, b) in toluene, and c) with droplets of various nonpolar liquids. d) Variation of transmittance of the TCMS- and TCMS/PFDTS-coated glass slides at 600 nm with the water concentration in toluene during TCMS coating. e) Image of the TCMS/PFDTS-coated glass slides on a piece of paper. The sample for (a)–(c) was prepared with C_{water} = 166 ppm.

coated glass slide without leaving a trace (Figure 4a; Supporting Information, Movie S3). The TCMS/PFDTS-coated glass slide was reflective in toluene and remained completely dry after taken out, which was direct evidence for the existence of the air cushion (Figure 4b; Supporting Information, Movie S1). This means that most of the area beneath the liquid droplet is a liquid–vapor interface, which indicates that the interaction between the liquid and the coating is very weak. This is also well evidenced by the following behavior of droplets of non-polar liquids on the TCMS/PFDTS coated glass slides: No observable deformation of the toluene droplets could be detected while moving the sample beneath the droplets and moving the droplets along the surface (Supporting Information, Movie S4). During CA measurements, the interfacial tensile force F_{n-l} between the needle and a small toluene droplet (ca. 2 μL, generated by evaporation of a larger droplet) could even overcome gravity of the droplet G_l plus the force F_{s-l} between the droplet and the sample surface (Supporting Information, Figure S5). The small toluene droplet (ca. 2 μL) could be easily picked up from the TCMS/PFDTS-coated glass slides by the needle. Furthermore, the droplets of toluene and decane could be operated freely on the surface.

The effects of the water content in toluene during silicone nanofilament growth and subsequent PFDTS coating could also be seen from changes in the transparency of the samples. The growth of silicone nanofilaments at low water concentrations leads to an antireflective property of the coating and could even increase the transmittance from 91.2% (bare glass slide) to about 94% at 600 nm (Figure 4d; Supporting Information, Figure S6). With increasing water concentration, the thickness and roughness of the silicone nanofilament layers increased, and then a decrease of the transmittance was observed. Modification of the nanofilaments with PFDTS resulted in a decrease of the transmittance, but a reasonable transparency was retained (Figure 4e). Transmission of the samples with nanofilaments grown at a water concentration of less than 124 ppm was more than 82% at 600 nm. The good transparency is attributed to the uniform growth of the nanofilaments (image at the bottom right corner of Figure 3), which decreases light scattering. The good transparency is remarkable because superoleophobic coatings require surface microstructures and roughness, which is in contrast to transparency.

Regarding the durability of the superoleophobic coatings, a series of experiments was carried out under various conditions (Supporting Information, Table S1). The results indicate that the coatings are stable against outdoor conditions, ozone, and strong UV light. After treatment at 200°C for 24 h, an improvement of superoleophobicity was even observed. No obvious changes of the CA and SA were detected after immersion in 1 M NaOH aqueous solution for 1 h. A slight increase of SA was observed after immersion in 1 M H_2SO_4 aqueous solution for 1 h. The coatings showed an excellent chemical and environmental stability; however, the mechanical stability still needs to be improved for some applications, as for other known superhydrophobic or superoleophobic coatings.

In summary, we have successfully fabricated superoleophobic surfaces with a high CA and ultralow SA for various nonpolar liquids by the combination of organosilanes in a simple grow-from method. The topography of the nanofilament layer plays an important role in influencing superoleophobicity of the surfaces and can be regulated simply by the water concentration in toluene during the TCMS coating procedure. Furthermore, the superoleophobic coatings show very good transparency and chemical and environmental durability. We believe that this technique could be used to prepare superoleophobic coatings on a variety of substrates and applied to various fields, as the silicone nanofilaments can be easily grown onto various substrates by a very simple procedure.

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