Lotus effect: smart windows

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ABSTRACT: The unique properties of plants as the lotus flower are known since ancient times, however, the principle behind this phenomenon has only been fully understood since the advent of nanotechnology in the late 20th century. Today, nanoscale coatings using the lotus effect enable dirt-repellant and self-cleaning properties. For the fabrication of these coatings, there are different materials and possibilities available; one being the so called sol-gel-process. A silica solution is brought directly onto a surface and afterwards undergoes a condensation reaction, forming nanoscale pillars on the surface. This pillar structure maximizes the interface with unfavorable interface energy. Additionally, it increases the overall surface which leads to the total free energy of water being lower if it stays in a droplet shape, thus creating a superhydrophobic surface. Superhydrophobic coatings can be applied to glass surfaces, thus creating "smart windows" with unique properties. These include a very efficient water repellence and dirt protection as particles are prevented from sticking on the surface and can easily be carried away by running water.

Introduction

The fact that the leaves of the lotus flower repel water and dirt in a unique way has been known since ancient days, it is widely recognized a symbol for faith and purity. In the past, it was tried to apply this self-cleaning effect to glasses and optical surface, therefore eliminating the need for regular cleaning. It is especially useful for surfaces that are hard to reach or in other ways too complicated to be cleaned regularly without greater effort.

It was originally believed that these properties were connected to friction; very even and uniform surfaces were believed to enhance water-repelling properties[i]. However, with new analysis methods as SEM, it was proven that in fact the contrary was the case.

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Wilhelm Barthlott and Christoph Neinhuis, from the University of Bonn, found out how certain leaves seemed to be able to protect themselves from external contamination. The following figure 1 shows a SEM-Image of the surface of a lotus leave. It is notable that that the leave exhibits a very rough structure, consisting of numerous, unordered pillars.
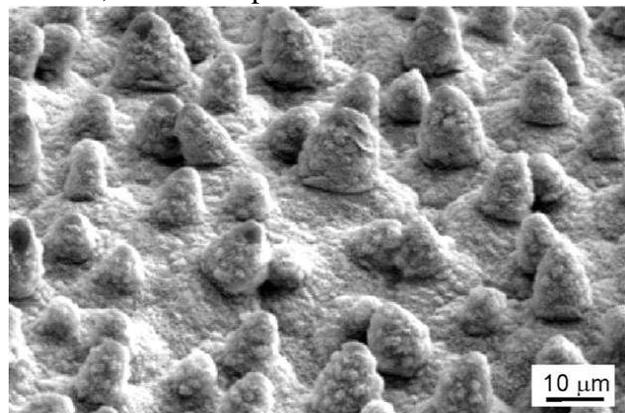

Fig. 1: Surface structure of a lotus leave[ii].

These pillars themselves possess a very rough structure on the surface made up of tetrapod-like wax crystals, increasing the overall roughness even more. The surface roughness is directly connected to the phenomenon of superhydrophobicity. How a surface behaves towards water, be it hydrophilic or (super-)hydropohobic, is defined by the contact angle between the surfaces of the substrate and the water droplet residing on it. For a contact angle θ < 90° the surface is hydrophilic. A hydrophobic behavior applies for 90° < θ < 180°. If θ > 150°, superhydrophobicity is achieved.

For the general calculation of the contact angle θ, *Young's equation* (1) is used:

$$cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$
(1)

The solid liquid interface tension is γ_{sl}, γ_{sv} is the surface tension of the solid material and γ_{lv} is the surface tension of the water droplet as illustrated in the following figure 2:
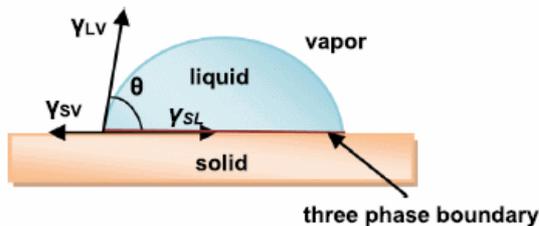

Fig. 2: Illustration of the contact angle and interfaces[iii].

It has to be noted that Young's equation is only fully viable for even surfaces.

When looking at rough surfaces, its roughness has to be considered by a roughness factor r which is the true surface divided by the theoretical flat surface.

For homogenous surfaces, the *Wenzel equation* (2) applies:

$$cos\theta_w = r \boxdot cos\theta$$
(2)

In this case, θ_w represents the contact angle for homogenously rough surfaces.

If looking at a heterogeneous surface where the water droplet is in contact with the surface as well as with gas enclosed in cavities, the contact angle θ_{CB} follows the *Cassie-Baxter equation* (3):

$$cos\theta_{CB} = r \boxdot cos\theta \boxdot f_{sl} - f_{lv}$$
(3)

The coefficients f_{sl} and f_{lv} represent the relative area fractions of the solid/liquid- and the liquid/vapour-interfaces, respectively.

For a surface to be self-cleaning, two more factors have to be taken into account: On the one hand, the roll-off angle, meaning the angle by which the surface is tilted, has to be lower than 10° and the droplet still be able to run down the surface. On the other hand, the tendency for dirt particles to stick has to be higher for the water droplet than for the surface for the dirt to be taken away[iv].

The most widely used production method for industrial superhydrophobic surfaces is the so called *sol-gel*-process. Its advantages are relatively low production costs, ease to use and apply and no limitation by are or product size where many other processes still struggle. It also produces surfaces with a high transparency while also reducing the reflectivity. Most other techniques have disadvantages or are simply not usable for industrial production. Plasma etching for example induces chemical impurities, whereas lithography is slow and not cost-effective[v].

The sol-gel-process follows three main steps: In the first step, a precursor molecule, basically the starting molecule for the process, is solved in a solution and thereby forms the *sol*. During the solvation, the precursor molecules, generally consisting of a metal with an organic rest, form hydroxyl end groups at the metal atom. The particles occur finely dispersed and show little to no tendency of coagulation. Afterwards, the sol is applied to a substrate. This is done via dip-coating: The substrate is dipped into the sol and then retracted with a constant speed. Through parameters like viscosity, density and surface tension the thickness of the coating layer can be tailored. In general, the higher these parameters, the thicker the layer. The retracting speed influences the thickness as well, a slower speed leads to a thinner layer. In this second step, the sol

condensates and forms a *gel*; the hydroxyl end groups react and form a link between two metal atoms via an oxygen atom. This creates a wide-meshed, crosslinked structure. In the mesh cavities, the solvent is still present. So in the final step, the solvent is dried out and a solid surface layer is achieved. For further enhancement of the desired abilities, this layer can optionally be coated with a functional epilayer[vi].

Experimental

In an experiment by Shang et al.[vii], three different sols were prepared to determine their hydrophobic behavior when applied to a glass substrate. Sol A consists of a mixture of tetraethylorthosilicate (TEOS) and methacryloxypropyltrimethoxysilane (MPS) in a ratio of 95:5, HCl was used as a catalyst. Sol B was prepared with TEOS and methyltrietoxysilane in a ratio of 1:1 with NH_4OH as a catalyst. Sol C consists of a mixture of TEOS and ethanol in water; again NH_4OH was used as a catalyst. All solutions were heated to 60 °C and stirred for a given time dependent on the precursor and catalyst to achieve a stable sol.

In the end, Sol A contained linear, silica-based polymer chains, Sol B highly branched nanoclusters and Sol C monosized silica, all finely dispersed in their respective solvents.

The glass substrates were cleaned in ethanol, sonicated and rinsed with deionized water before the coating process. The coating itself was achieved via dip-coating. To remove the residual solvent after the coating, all samples were dried for 5min and then heat-treated at 110 °C for an hour. After the treatment, the surface layers were subjected to oxygen plasma etching to remove CH_3-end groups, followed by cleansing with deionized water. As a final step, the films were coated with a *self-assembly monolayer* consisting of tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (TFCS) which form covalent bonds with the silicon atoms of the solid surface. The surface topology of the epilayer was characterized via an atomic force microscope (AFM), the contacts angles were determined via optical microscopy and a goniometer whereas the transmit-

tance and reflectance were measured with a spectrometer.

Results & Discussions

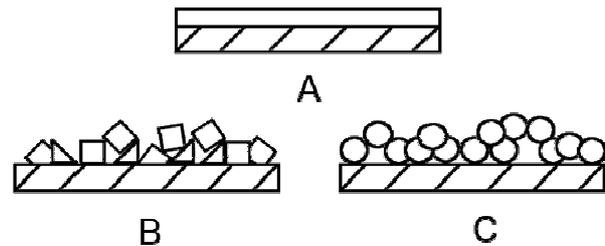The different sols lead to three different surface structures as shown in figure 3 below:

Fig. 3: Surface structures of the different sols.

Sol A (linear silica-polymer chains) formed a homogenous, smooth film on the substrate. Sol B (branched nanoclusters) formed a very rough surface with a lot of edges and cavities. A similar roughness was achieved for sol C, but in this case, the structure consists of spheres of similar size, reducing the number of edges and sharp cavities drastically. The spheres also show a certain porosity on their respective surfaces. However, these layers alone are still hydrophilic. The coating with TFCS leads to a coverage with CF_3 end groups as shown in the following figure 4:
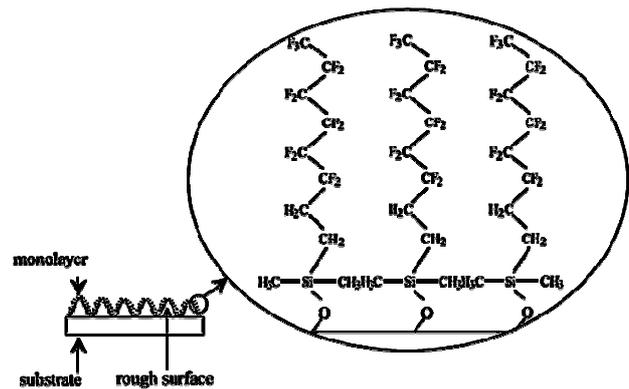
Fig. 4: Schematical view of the TFCS monolayer[vii].

The fluorine atoms are each surrounded by three free electron pairs which lead in combination with the high electronegativity to a very highly charged surface. These charges are so strong that they completely repel any water molecule comes

close to the surface. The following table 1 shows the results of the measurements of the contact angles and the roughness factors of the different samples. Measured were the angles of the coated substrate prior to the etching and coating (θ_{sub}), the contact angle after coating with TFCS (θ_{TFCS}) and the roughness factor r of the surface.

Tab. 1: Contact angles and roughness factors[vii].

Sol layer	$\theta_{sub}/°$	$\theta_{TFCS}/°$	r
A	17	118	1
B	83	125	1.02
C	15	150	1.013

Before the coating with TFCS, all angles were below 90°, indicating hydrophilic behaviour. Sample A showed a low contact angle of 17° which could be increased to 118 ° after the coating with TFCS. This means hydrophobic, but not superhydrophobic behaviour. The roughness factor of one also proves a completely smooth surface. In the case of sample B, the contact angle prior to the coating is relatively high due to the high roughness but mainly to the fact that the surface is covered with CH_3 end groups that repel water much stronger than the surfaces of samples A and C. The contact angle after the coating is only slightly bigger than of sample A which seems surprising when looking at the roughness factor which is the highest of all three samples. But when looking at the structure (see Fig. 2), it is evident that the structure's roughness prevents a complete and gapless coating of the surface with TFCS which leads to the low increase of the contact angle in comparison to sample A. Sample C shows the lowest contact angle prior to the coating due to the fact that is has to be calculated via the Wenzel-equation (2) and therefore the roughness coefficient increases the hydrophilic behaviour at first. After the TFCS coating however, the sample shows the biggest contact angle of all and with that also superhydrophic behaviour. The roughness factor is not as high as sample B, but due to the structure, a complete coating with TFCS is possible. It has to be noted that due

to the roughness and the coating, for both samples B and C, the area fraction f_{lv} has to be taken into account. The fluorine end groups increase the energy of the water/solid interface and therefore make it unfavourable for the water to wet the solid surface. This leads to a heterogenous surface and require a calculation via the Cassie-Baxter equation (3) Because of an increase of f_{lv}, the contact angle increases as well.

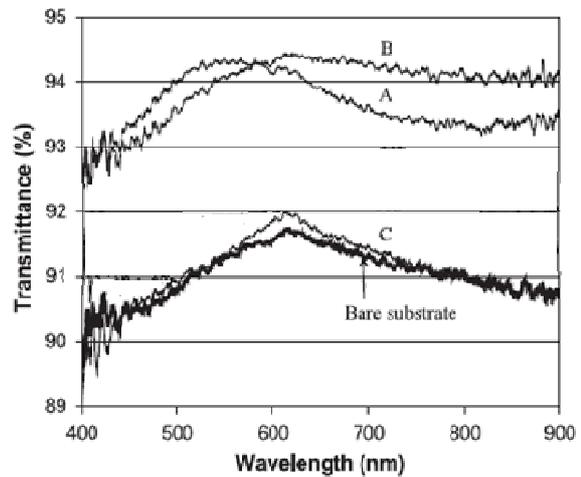The results of the transparency measurements are shown in the following figure 5:

Fig. 5: Light transmittance of the coated samples[vii].

All samples show a transmittance over 90 %; it is also interesting to note that the coatings increase the transmittance in comparison to the bare substrate. Sample B shows the highest transmittance with A being close but lower in the higher wavelength area. Sample C however lies more in the transmitting range of the bare substrate. In general, the higher transmittance is most likely caused by the decrease of reflectance on the surface. To illustrate this decrease, the following figure 6 shows the results of the reflectance measurements plotted against the wavelength (AB and AC are of no importance to this discussion):
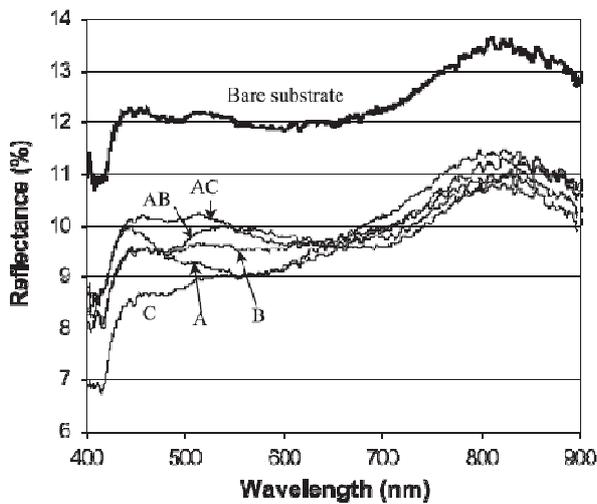
Fig. 6: Light reflectance of the coated samples[vii].

It can be clearly seen that all coated samples show a reduced reflectance in comparison to the bare substrate. It also has to be noted that it is quite similar for all three samples. Optical and self-cleaning glasses are only transparent if the surface structures are smaller than the wavelength of visible light. This explains the smaller transmittance of sample C in comparison to A and B even if they show a similar reflectance. For sample C, the surface porosity of the silica spheres leads to scattering of light which occurs in addition to transmittance and reflectance.

Conclusion

The experiment shows that transparent, superhydrophobic surfaces can be manufactured via sol-gel coating of glass substrates if an epilayer of TFCS is used. However, the water-repelling properties depend strongly on the sol used and only one in the experiment brought the desired effect. Only sample C, the surface coated with monosized silica, showed superhydrophobic be-

haviour. To achieve self-cleaning abilities on "smart windows", this would be the most favourable choice due to the best water-repelling and high transparent properties.

It remains to be seen how the coating behaves in a situation subjected to wear and radiation, however. In everyday use, mechanical abrasion and UV light will affect the surface coating and most likely diminish the hydrophobic and self-cleaning properties after longer periods of use.

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