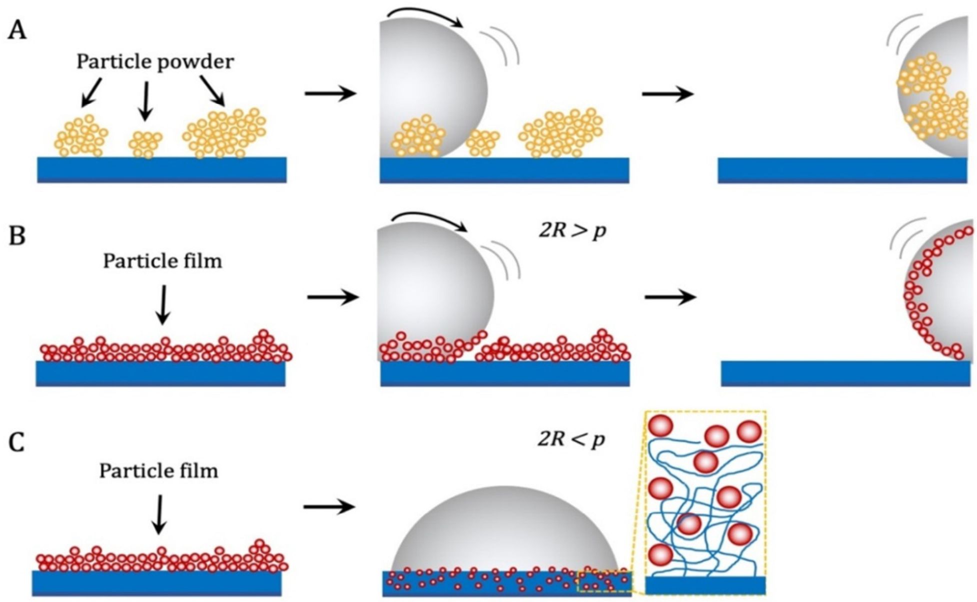
How dynamic contact angel measurements can help to understand self-cleaning surfaces

Dirt-repellent and easy-to-clean surfaces are getting more and more important for the new smart products and for the optimisation of different technological processes.

Self-cleaning surfaces can be divided into three categories: superhydrophobic surfaces, superhydrophilic surfaces and photocatalytic surfaces. Superhydrophobic surfaces are dirt- and water-repellent, superhydrophilic surfaces let the water film with solid particles slide down easily and photocatalytic coatings chemically break down dirt when exposed to light. Despite the commercialization of superhydrophobic coatings, the fundamental mechanisms of their self-cleaning processes are still unclear.

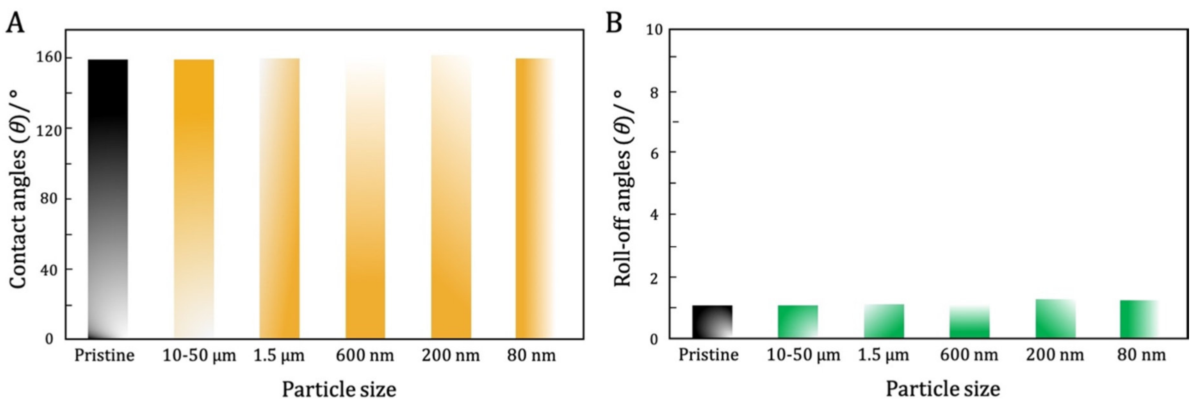
Butt, Vollmer et al. recently presented a nanoporous superhydrophobic surface with self-cleaning function, and successfully described the working mechanism of the self-cleaning process on the micrometer scale. The authors developed a well-designed superhydrophobic surface that can resist high contamination ratio, including both hydrophobic and hydrophilic nanoparticles and indicated the pore size of the surface coating as the key factor of the contamination resistance.

For the experiments glass slides coated by silicone nanofilaments were used as model surface. To simulate hydrophobic contamination, such as soot or dust, the nanoporous superhydrophobic surfaces were contaminated with various hydrophobic particles (**Scheme 1, A**). After that the surfaces were rinsed with water drops to remove the particles.



Scheme 1: *Schematic illustration of the self-cleaning process of (**A**) hydrophobic particle powders (yellow), (**B**) hydrophilic particle film (red, 2R > p) and (**C**) hydrophilic particle film (red, 2R < p) by a water drop (gray) on a superhydrophobic surface (blue). R: Particle diameter; p: Surface pore diameter*

Picture 1 shows all surfaces contaminated by hydrophobic particles with low roll-off (< 2°) and high contact angles (> 150°) after self-cleaning. Static contact angles and roll-off angles were measured using the DataPhysics OCA 35 optical contact angle measurement device.

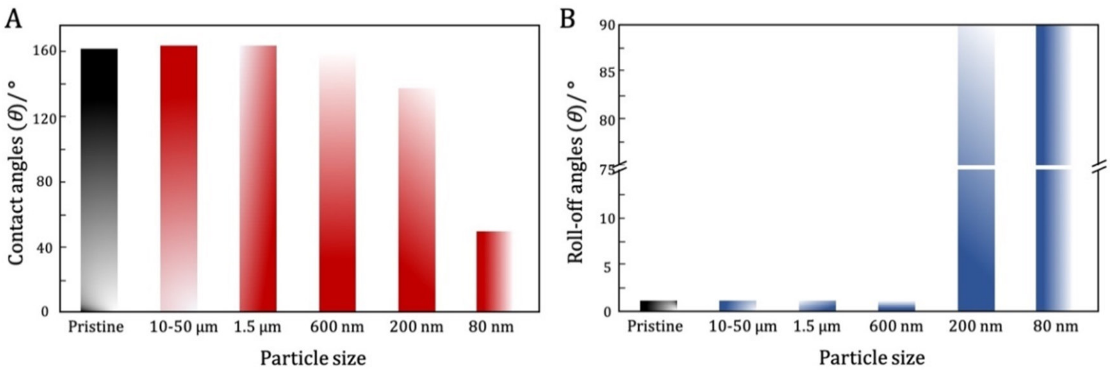


Picture 1: *Static contact angles and roll-off angles after self-cleaning of a superhydrophobic surface contaminated with hydrophobic particle powders*

To simulate the most severe contamination, the surfaces were treated with various hydrophilic particles dispersed in ethanol (**Scheme 1, B, C**).

The results are presented in **Picture 2** and lead to the following conclusions:

- The 10- to 50-µm and 1.5-µm particles ($2R > p$) could not enter the coating, and they were removed easily by water droplets.
- Most of the 600-nm particles ($2R \sim p$) were also removed, and the surfaces showed low roll-off (< 2°) and high contact angles (> 150°).
- The 80- and 200-nm particles ($2R < p$) could enter, dry out within the pores, and lead to the failure of self-cleaning. The contact angles decreased to around 40° and 140°, respectively, and the roll-off angles increased above 90°. In this case, the pore size of the coating should be designed as small as possible to get higher contamination resistance.



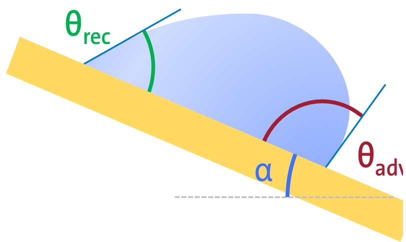
Picture 2: *Water contact and roll-off angles after self-cleaning of a superhydrophobic surface contaminated with various hydrophilic particles (dried from ethanol dispersion)*

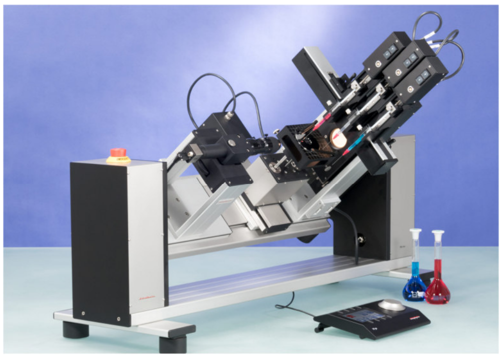
For the deeper understanding of the cleaning mechanism the authors monitored the interaction between hydrophilic or hydrophobic 10- to 50-µm particles on a nanoporous superhydrophobic surface and 10-µl drops by laser scanning confocal microscopy (LSCM). They found that the drop lifted the particles from the surface like a layer on the drop surface forming a so-called liquid marble; and quantified the forces involved in the self-cleaning process. Furthermore, polyester fabrics coated by nanoporous superhydrophobic surfaces were applied on a car (fabrics were fixed on the front, rear side, back windows, and side mirror; location: Rhineland-Palatine area in Germany, periods: 257 days, temperatures: −10-32°C, humidities: 40-100%). No nanocontamination between the nanofilaments was found even after exposing the surfaces to high ultraviolet radiation, rain, frost, icing, insects and dirt. An industrial dirt pickup simulation test for paints and coatings from Evonik Resource Efficiency GmbH verified the good self-cleaning property and the high contamination resistance compared with the bare fabrics and benchmark surfaces.

Determination of the Roll-Off Angle

The **roll-off angle** indicates how much a surface needs to be **inclined α to let a drop on its surface roll-off**. The roll-off angle is highly dependent on the measuring conditions, such as drop size and tilt speed. In order to measure the roll-off angle precisely and reproducibly it is thus important to work with an electronic tilting system such as our **TBU 100** which allows for a precise control of tilting speed and angle α.

Drops are usually deformed before rolling of resulting in deformed drops that then slide over the surface. The deformation of the drops leads to an **advancing θ_{adv} and receding contact angle θ_{rec}**. The difference of these angles is the so called **contact angle hysteresis** which is a measure for the roughness and inhomogeneity of the surface.





Overall, this paper presents a nanoporous superhydrophobic surface with high contamination resistance as proven in a real-world test environment (on the car windows) and industrial testing scenarios. The authors emphasized that the pore sizes of the coating plays a major role in the self-cleaning process. Surfaces based on nanofilaments with a pore size below 500 nm could withstand most kinds of particulate contamination (sizes: 600 nm-50 µm). This research thus offers considerable advantages in the fabrication of self-cleaning superhydrophobic surfaces.

The optical contact angle analyzer OCA 35 (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

When and how self-cleaning of superhydrophobic surfaces works; Florian Geyer, Maria D'Acunzi, Azadeh Sharifi-Aghili, Alexander Saal, Nan Gao, Anke Kaltbeitzel, Tim-Frederik Sloot, Rüdiger Berger, Hans-Jürgen Butt, Doris Vollmer; *Sci. Adv.* **2020,** 6, eaaw9727; DOI: 10.1126/sciadv.aaw9727