# Superhydrophobic Surfaces

*Edited by* A. Carré K.L. Mittal





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Edited by A. Carré and K. L. Mittal



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### Preface

For many years smooth surfaces with appropriate surface chemistries (e.g., fluorinated polymers, silicone resins, self-assembled monolayers of alkyl or fluoroalkylsilanes) have been known to exhibit an 'intrinsic hydrophobicity' with water contact angles of up to  $120^{\circ}$ . Superhydrophobic (also sometimes called ultrahydrophobic) surfaces refer to considerably higher contact angles (>150°) and they can only be achieved through the combination of hydrophobicity with appropriate surface texture or roughness. For 'roll-off' superhydrophobicity (resulting in self-cleaning) the advancing contact angle should be as high as possible (ideally 180°), receding angle should be as high as possible (ideally 180°). This will result in a tilt angle of 0°.

In nature there are many impressive and elegant examples of superhydrophobic surfaces. The most widely known example is the lotus leaf because of its selfcleaning action: rain drops bounce off after impact, then entirely roll off the lotus leaf and drag along any dirt particles without leaving residues. Concomitantly, the lotus leaf is revered in many civilizations as it represents a sign of purity. Superhydrophobicity in nature is not limited to just lotus leaves. Several other plants, animals and insects possess superhydrophobic properties. Water striders can easily stand and walk on water due to the special non-wetting feature stemming from the legs' special hierarchical structure. Another example will be the easy roll-off of water droplets from the surface of butterfly wings. Certain animals or insects thrive on superhydrophobicity to collect water from the morning dew for subsequent use.

Learning from nature, there are essentially two different approaches to achieve superhydrophobic surfaces: either depositing a low surface energy coating on an appropriately roughened (textured) surface, or by roughening a low surface energy material. The putative view is that a hierarchical structure (micro and nanoscales) is necessary to achieve superhydrophobicity. Thus artificial design of superhydrophobic surfaces constitutes an excellent example of biomimetic materials.

Even a cursory look at the literature will evince that in the last few decades there has been an explosive interest in the arena of superhydrophobic surfaces. This stems from the fact that superhydrophobic materials are intrinsically fascinating to study coupled with their myriad of applications which include, e.g., as water-proof,

#### Preface

anticorrosive, self-cleaning and stain-resistant surfaces (for solar panels, displays, windows, paints and fabrics) or as surface treatment to reduce viscous drag in small channels used for micro/nanofluidic applications such as lab-on-chip devices or in reducing resistance to transport of liquids through pipes. As a result, many different approaches have been reported to design superhydrophobic surfaces from many diverse materials (polymers, metals and other inorganic materials, composites, textiles, paper).

So in light of the current intense research activity and interest in the domain of superhydrophobic surfaces, and all signals indicate that this high tempo of activity will continue unabated, we decided to bring out this special volume, which reflects the cumulative wisdom of many world-renowned researchers in this burgeoning field.

This book is based on the three *Special Issues of the Journal of Adhesion Science and Technology (JAST)*: Vol. 22, Nos 3–4, pp. 231–402 (2008); Vol. 22, No. 15, pp. 1799–1984 (2008); and Vol. 23, No. 3, pp. 381–512 (2009) dedicated to this topic. Based on the widespread interest and tremendous importance of superhydrophobic surfaces, we decided to make this book available as a single and easily accessible source of information. The papers as published in the above-mentioned Issues have been re-arranged in a more logical fashion in this book.

This book contains a total of 34 papers (reflecting overviews and original research) covering many ramifications of superhydrophobic surfaces and is divided into five parts as follows: Part 1: Fundamentals of Superhydrophobicity; Part 2: Superhydrophobic Surfaces from Polymers; Part 3: Superhydrophobic Surfaces from Silanes, Colloids, Particles or Sol-Gel Processes; Part 4: Superhydrophobic Surfaces from Electrochemical Processes; and Part 5: Applications and New Insights. The topics covered include: fundamental understanding and mechanisms of superhydrophobicity; various strategies for fabricating superhydrophobic surfaces from a large diversity of materials (polymers, metals and other inorganic materials, composites, textiles, paper) using a wide spectrum of processes ranging from very simple to very sophisticated (lithographic techniques, plasma treatment, electrochemical processes, self-assembly processes, colloidal particles, sol-gel processes, nanofilaments, coating deposition, and simple scraping); static and dynamic characteristics of nanopatterned surfaces; superhydrophobic micro- and nano-structured surfaces; superhydrophobic materials based on micro- and nanofibers; superhydrophobic nanofilament coatings; UV-resistant and self-cleaning surfaces; environmentally responsive wettability behavior; various applications of superhydrophobic surfaces including superhydrophobic textile surfaces, superhydrophobic coatings for microdevices, electrowetting on superhydrophobic surfaces, wetting of surfactant solutions on superhydrophobic surfaces; and understanding the mechanism of water strider leg and its walking on water. It is quite patent that both fundamental and applied aspects of superhydrophobic surfaces as well as their many ramifications are accorded due coverage in this book and, concomitantly, this book represents a comprehensive treatise on this fascinating subject.

We certainly hope that this book containing bountiful up-to-date information will be of great interest and value to anyone interested (peripherally or centrally) in this wonderful area of superhydrophobic surfaces. This book should serve as a gateway for the neophyte and a commentary on current research for the veteran researcher. We further hope that this book will serve as a fountainhead for new research ideas and as we explore superhydrophobic surfaces further and devise ways to enhance their robustness and longevity, more application vistas will emerge.

### Acknowledgements

Now comes the pleasant task of thanking those who helped in materializing this book. First and foremost our thanks go to the authors for their interest, enthusiasm, cooperation and contribution without which this book would not have seen the light of day. We profusely thank the unsung heroes (reviewers) for their time and efforts in providing many valuable comments as comments from peers are *sine qua non* to maintain the highest standard of a publication. Finally, our appreciation goes to the appropriate individuals at Brill (publisher) for giving this book a body form.

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### Part 1

### **Fundamentals of Superhydrophobicity**

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### **Fabrication of Superhydrophobic Surfaces**

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#### Abstract

Superhydrophobicity has recently drawn a great deal of attention from both fundamental and practical application points of view. This paper summarizes the basic principles involved in creation of superhydrophobicity and reviews the diverse methods recently developed to make superhydrophobic surfaces and coatings. The hydrophobic property of materials can be amplified through the surface roughness. This was first addressed theoretically in the 1930s and 1940s. Although there have been significant advances made in superhydrophobicity theories, the basic design principles to fabricate superhydrophobic surfaces and coatings remain essentially the same. Recent developments in fabrication of superhydrophobic surfaces can be categorized in three different strategies — (1) roughening hydrophobic surfaces, (2) creating rough topographic features on substrates followed by application of hydrophobic surface modification methods and (3) depositing hydrophobic materials with rough surface textures. Various methods found in the literature are grouped and described in these categories. Finally, future challenges and issues involved in utilizing and understanding superhydrophobicity are discussed.

#### Keywords

Superhydrophobic surfaces, principles, fabrication

### 1. Introduction

Superhydrophobicity has recently drawn a great deal of attention from both fundamental and practical application points of view. Although superhydrophobicity has been studied since the mid-1930s, interest in this phenomenon have grown substantially in the past few years due to recent recognition of its potential applications in various areas. If superhydrophobic properties are imparted to fabrics, one can make weather resistant fabrics and garments. If glass or display surfaces are made superhydrophobic, they will be resistant to water condensation and exhibit an antifogging capability. These materials could be useful for vehicle windshields, display panels, etc. If water droplets fall on a superhydrophobic surface, they will easily slide off the surface and remove dust particles along their sliding pathway. This property (so-called self-cleaning) is desirable for outdoor optical devices such as

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#### S. H. Kim

solar cell panels or satellite dishes. The water repellency can also be used to move liquids in contact with the surface with no or reduced drag. This property could be used for drag reduction in microfluidics, piping, or boat hulls. With these application potentials, various ways of producing superhydrophobic surfaces as well as scientific understanding of superhydrophobic behavior have recently been developed [1–4]. The scope of this paper is to briefly review the basic principles of superhydrophobicity and summarize different strategies for producing superhydrophobic surfaces and coatings.

### 2. Fundamental Principles Behind Superhydrophobicity

Let us consider a liquid drop suspended in a gas phase. The shape of liquid drop is determined by two factors — surface tension at the liquid–gas (vapor) interface  $(\gamma_{LV})$  and gravity. The surface tension force acting on the liquid drop tends to impose a minimal surface area, making the drop spherical. This force scales as  $\gamma_{LV} \times d$ (where *d* is the diameter of liquid drop). Meanwhile, the gravitational body force imposed on the liquid tries to flatten the liquid. This force scales as  $\rho g d^3$  (where  $\rho$  is the liquid density and *g* is the gravitational acceleration constant). The body force can be neglected if the liquid drop size is smaller than the so-called capillary length,  $\kappa_c$ :

$$\kappa_{\rm c} = \sqrt{\frac{\gamma_{\rm LV}}{\rho_g}}.$$
(1)

The capillary length for clean water at ambient conditions is  $\sim 2.7$  mm. In other words, when the liquid drop is smaller than this capillary length, the gravitational effect is negligible and can be ignored in prediction of the equilibrium shape of liquid.

When a small liquid drop (diameter  $< \kappa_c$ ) is placed on an ideal (i.e. chemically and topographically homogeneous) solid surface, its shape is now changed due to the introduction of a new interface — three-phase contact line (Fig. 1). In this situation, each of the solid–liquid, liquid–gas and solid–gas interfaces draws the contact line so as to minimize the corresponding total surface free energy. Balancing these



Figure 1. Equilibrium contact angle of liquid on a flat surface (Young's equation).

interfacial tensions on the tangential direction of the non-deformable solid surface yields an equilibrium relation (Young's equation):

$$\gamma_{\rm SL} + \gamma_{\rm LV} \cos \theta_{\rm Y} = \gamma_{\rm SV},\tag{2}$$

where  $\gamma_{SL}$ ,  $\gamma_{LV}$  and  $\gamma_{SV}$  are the solid–liquid, liquid–gas and solid–gas interfacial tensions, respectively, and  $\theta_{Y}$  is the equilibrium contact angle. So, for small liquid drops on solid surfaces, the contact angle of liquid ( $\theta_{Y}$ ) is often enough to describe the liquid drop shape and wettability.

In reality, few solid surfaces are truly homogeneous. When the surface contains some microscopic roughness, the tangential direction at the three-phase contact line is not parallel to the apparent (macroscopic) solid surface. The first attempt to understand the correlation between the surface roughness and apparent contact angle was made by Wenzel (1936) [5]. He noticed that the hydrophobicity of a material was enhanced by the presence of surface textures and attributed this behavior to the increase of the effective surface area. He then introduced a dimensionless roughness factor,  $r_s$ , which is defined as the ratio of the actual surface area over its nominal (apparent) surface area. Assuming that water conformally fills the surface texture, he derived the equilibrium condition for the surface with a roughness  $r_s$  [5, 6]:

$$\cos\theta_{\rm W} = r_{\rm s}\cos\theta_{\rm Y},\tag{3}$$

where  $\theta_W$  is the apparent water contact angle in the so-called Wenzel state (Fig. 2a). This equation predicts that the water contact angle higher than 90° on a flat surface can be further increased by roughening the solid surface since the roughening in-



**Figure 2.** Amplification of hydrophobicity due to surface roughness. In the Wenzel model, the liquid conformally follows the surface topography (a), while in the Cassie–Baxter model, the air remains in the lower regions of the topographic features (b). In (a),  $r_s$  represents the ratio of the actual surface area of the rough substrate to the nominal surface area. In (b),  $f_s$  is the solid fraction that is in contact with the liquid under the droplet.

creases  $r_s$  (>1). For flat surfaces ( $r_s = 1$ ), the Wenzel equation (3) gives the Young's equation (2).

As the surface roughness (height-to-area aspect ratio of surface topographic features) increases, it becomes difficult for the liquid to conformally fill the surface texture. This is easily predictable since a hydrophobic material has a higher surface energy when it is wet with water ( $\gamma_{SL}$ ) than when it is dry ( $\gamma_{SV}$ ). In order to lower the surface energy, air can remain inside the texture (Fig. 2b). Since the contact angle of liquid on air ( $\theta_{LV}$ ) is 180°, air entrapment will increase the hydrophobicity further. In this situation, the water drop is now viewed as sitting on a composite surface consisting of solid and air. At the minimum of surface energy and using Young's equation, the apparent contact angle for this case has been described by Cassie and Baxter as [7, 8]:

$$\cos\theta_{\rm CB} = f_{\rm s}\cos\theta_{\rm Y} + f_{\rm v}\cos\theta_{\rm LV} = f_{\rm s}\cos\theta_{\rm Y} - (1 - f_{\rm s}),\tag{4}$$

where  $\theta_{CB}$  is the apparent water contact angle in the so-called Cassie–Baxter state (Fig. 2b) and  $f_s$  and  $f_v$  are the fractions of solid and vapor (air) contacting the liquid  $(f_s + f_v = 1)$ . Increasing surface roughness decreases  $f_s$ , which results in a large increase in  $\theta_{CB}$  (much larger than  $\theta_W$ ).

Although there is no clear boundary between these two states, the apparent water contact angle is generally expected to follow the Wenzel behavior on surfaces with mild roughness and to obey the Cassie–Baxter behavior on highly rough surfaces. On hydrophobic surfaces ( $\theta_{\rm Y} \sim 100^{\circ}$ ) of moderate roughness ( $r_{\rm s} \sim 2$ ), both Wenzel and Cassie–Baxter states can co-exist [9–12]. For example, depositing a water droplet on a moderately rough surface can lead to the Cassie–Baxter state with air pockets in the surface texture. When the water droplet is produced by vapor condensation, the Wenzel state is more likely to be formed [13]. When the Cassie–Baxter state can also occur [13–15].

Besides high static water contact angles, the easy sliding-off behavior of liquid droplet is another criterion related to superhydrophobicity. The sliding behavior of the droplet is again governed by the balance between surface tension and gravity. On a tilted surface, the liquid drop becomes asymmetric and the contact angle of the lower side becomes larger and that of the upper side gets reduced (simple mass conservation principle). The difference between these two contact angles (hysteresis) reaches the maximum when the liquid drop begins to slide down the tilted surface. The contact angles of forefront and trailing edges of the liquid drop just prior to movement of its contact line are called the advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) contact angles, respectively. When the gravity acting on the liquid drop becomes larger than the surface tension force ( $F_{retention}$ ) caused by the contact angle which is holding the liquid droplet from sliding (Fig. 3), the liquid droplet starts sliding. So, the critical angle ( $\alpha$ ) for water droplet to slide off the surface can be calculated by balancing these two forces [16–18]:

$$\gamma_{\rm LV}(\cos\theta_{\rm r} - \cos\theta_{\rm a}) = \frac{mg}{w}\sin\alpha,\tag{5}$$

 $F_{\text{retention}} = \gamma_{\text{LV}} \left( \cos \theta_{\text{r}} - \cos \theta_{\text{a}} \right)$ 



Figure 3. Surface tension force due to contact angle hysteresis holding the liquid droplet from sliding on a tilted surface.

where m and w are the droplet mass and the solid–liquid contact width, respectively. This equation predicts that for a given mass of water droplet, a smaller contact angle hysteresis will result in a smaller sliding angle and easier roll-off.

A simple geometric analysis predicts that it is difficult to roll off a liquid droplet from the surface if the static apparent contact angle is low (<140°) unless the contact angle hysteresis is very small (<4–5°) [2]. It is not easy to obtain low contact angle hysteresis for surfaces with low contact angles. In the rich literature on superhydrophobicity, the only example found to meet this criterion is flat silicon oxide surfaces treated with siloxane molecules that have bulky side groups and easy rotation along the molecular axis [19]. On the other hand, a liquid droplet will easily roll off if the apparent contact angle is larger than ~150°, even if the contact angle hysteresis is larger than 5° [2]. This is due to the reduction of the solid–liquid contact (small w). When water droplets roll over the surface, they can easily trap and remove dust particles from the surface. Due to this reason, a superhydrophobic surface is often called "self-cleaning" since the rolling-off of water droplets keeps the surface clean.

The Wenzel state tends to give a larger contact angle hysteresis than the Cassie–Baxter state. As the contact line recedes, some liquid can be trapped in the surface texture if the liquid is conformally filled in the texture initially. This can decrease the receding contact angle significantly, resulting in a large contact angle hysteresis and thus in a large critical sliding angle [20]. This liquid trapping in the surface texture is not expected for the Cassie–Baxter state; so the contact angle hysteresis and critical sliding contact angle are much smaller than the Wenzel state. In other words, the water droplet runs off easily on Cassie–Baxter state, it has been shown that the ones with poor continuity of the three-phase contact line are most preferable to give a low critical sliding angle [21].

From these basic principles, one can identify two key requirements to obtain superhydrophobicity (high water contact angle and small contact angle hysteresis). One is proper surface chemistry and the other is proper surface roughness. On flat surfaces, the highest water contact angle that can be obtained is about  $115-120^{\circ}$  on poly(tetrafluoroethylene) or fluorine-terminated organic surfaces. By preparing surfaces with appropriate roughness and hydrophobic chemistry, water contact angles higher than  $150^{\circ}$  and easy water run-off can be attained. This is a central guideline in designing superhydrophobic surfaces. The readers interested in more advanced-level superhydrophobic principles are suggested to refer to recent publications by a number of researchers [10, 11, 15, 21–27].

### 3. Fabrication of Superhydrophobic Surfaces and Coatings

### 3.1. Natural Superhydrophobic Surfaces

Many superhydrophobic examples can be found in nature. One of the most well known examples is lotus leaves. High resolution scanning electron microscopy (SEM) study of the lotus leaf reveals that the leaf surface contains randomly distributed papillae (bumps) at a scale of 5–10 µm which consist of hairy nanostructures with a typical diameter of 100–200 nm (Fig. 4) [28, 29]. These complex surface textures consisting of micro- and nano-scale hierarchical structures amplify the hydrophobicity of the epicuticular wax film at the leaf surface to attain a water contact angle of 150–160° and a critical sliding angle lower than ~2°. In this way, the leaf surface can always be kept clean to maximize the uptake of sun light. Other plants with superhydrophobic leaves include tulipa, iris, asphodelus, drosera, eucalyptus, euphorbia and gingko biloba [28, 30].

Superhydrophobic surfaces can also be found in insects and birds. For example, water striders have non-wetting legs that allow them to walk on water (Fig. 4) [31]. SEM imaging of the water strider leg found micro-scale setae which contain nanoscale grooves at the surface. Once again, these micro- and nano-scale hierarchical structures together with the hydrophobic wax renders superhydrophobicity needed to walk on water freely. The wings of butterflies and cicadae exhibit superhydrophobicity [32, 33]. The superhydrophobicity of these wings is believed to keep the wing surface water droplet free and prevent them from sticking together. While these insects use superhydrophobicity to remove water droplets from their body, Nambibian beetles use superhydrophobicity for a different purpose — collecting water droplets rather than repelling them [34]. The Nambibian beetle has superhydrophobic tracks around hydrophilic elytrae. When water droplets are formed from morning dew or fog at the hydrophilic elytrae, these droplets are rolled down to the mouth through the superhydrophobic track. In this way, these beetles can get water in a desert environment. The feathers of many birds living on water are superhydrophobic. When these birds come out of water, water droplets are immediately removed from the body due to the superhydrophobicity of their feathers.



**Figure 4.** SEM images of naturally superhydrophobic surfaces: (a, b) lotus leaf and (c, d) water strider leg (reprinted with permission from Wiley Interscience [29] and Nature Publishing Group [31]).

### 3.2. Synthetic Superhydrophobic Surfaces

The key recurring theme of all the examples found in nature is that hydrophobicity is amplified to superhydrophobicity by surface textures. These textures often consist of micro- and nano-scale hierarchical structures (Fig. 4) [29, 31]. This dual-scale roughness is required for both high water contact angle and low sliding angle [35]. Based on these principles, various synthetic approaches have been developed for preparation of superhydrophobic surfaces and coatings by combining hydrophobic chemistry and geometric effects (Fig. 5) [36].

A very early example of synthetic superhydrophobic materials can be found in a patent filed in 1945 [37]. Norton prepared superhydrophobic fabrics by dipping textiles (intrinsically rough due to woven structure of fine threads) in a toluene solution of 4 wt% methylsilicone followed by drying at 100°C. The fabrics processed in this way gave water contact angles higher than 150°. The first systematic study of the roughness effect on advancing and receding water contact angles was made by Johnson and Dettre in 1964 [20]. They sprayed waxes on flat glass substrates and controlled the surface roughness through post-spray heat treatments. Using these samples, they showed that the advancing contact angle increases continuously with surface roughness reaches a critical value at which the receding angle suddenly jumps to a value close to the advancing angle. Later, this behavior was interpreted as



**Figure 5.** Optical images of water droplets ( $\sim 2 \text{ mm}$  diameter) on a superhydrophobic coating deposited on (a) gold film, (b) Si wafer, (c) Kimwipe<sup>®</sup> tissue and (d) cotton (reprinted with permission from American Chemical Society [36]).

a transition from the Wenzel state to the Cassie–Baxter state. Systematic studies of advancing and receding contact angles of various test liquids on more sophisticated surfaces were made by Onda, Shibuichi, Satoh and Tsujii at the Kao Corporation in 1996 [38, 39]. In these experiments, they produced superhydrophobic surfaces by coating fluorinated silanes onto anodized aluminum surfaces and by growing fractal structures of alkyl ketene dimer wax. Since then, the number of engineered ways to fabricate superhydrophobic surfaces and coatings has been skyrocketing in the scientific literature. The synthetic strategies used in these recent efforts are summarized in the following three sections.

### 3.2.1. Roughening Hydrophobic Materials

Due to their low surface energy, fluorinated polymers intrinsically exhibit strong hydrophobicity. For example, the water contact angle ( $\theta_{\rm Y}$ ) on flat poly(tetrafluoroethylene) (PTFE) surfaces is typically 115–120°. Roughening these polymer surfaces leads to superhydrophobicity. One of the most widely used methods for fluorinated polymers is plasma etching. The high-energy oxygen species generated by plasma can randomly etch fluorinated polymer materials and create surface roughness needed to increase the water contact angle to ~170° [40, 41]. The PTFE surface can also be roughened by simply stretching [42]. The surface of PTFE films stretched more than 100% of its original length consists of submicrometerdiameter fibrous crystals with a large fraction of void space in the surface. Another way is to use micro-phase separation of fluorinated block copolymers. The microphase separation of block copolymers can create a variety of nanoscale features needed for generation of superhydrophobicity. For example, a copolymer having equimolar amounts of fluorinated acrylate and methyl methacrylate monomers develops hexagonally-packed nanoscale pores at the cast film surface during drying from solution under certain humidity conditions [43]. By controlling film deposition parameters, the pore size much smaller than the light wavelength can be produced, making the cast film optically transparent.

Poly(dimethylsiloxane) (PDMS) is a hydrophobic polymer that can easily be processed to make rough textures at the surface. A high power laser abrasion process has been employed to make micro- and nano-scale structures. PDMS surfaces processed with laser abrasion have shown a water contact angle higher than 160° and water sliding angle much lower than 5° [44, 45]. Since PDMS can also be processed as an oligomeric liquid form and then cured into an elastic solid by UV irradiation, it is widely used to replicate surface textures of a mold and to make a stamp in soft lithography. This process has been utilized to replicate the structure of lotus leaves and produce superhydrophobic PDMS surfaces [46].

Roughening the surfaces of hydrophobic hydrocarbon materials can impart superhydrophobic properties. In 1953, Bartell and Shepard [47] demonstrated that superhydrophobicity could be created by roughening paraffin surfaces through machining. Like PTFE, plasma etching can be used to create roughness and obtain superhydrophobicity on the surface of hydrocarbon polymers such as polypropylene [48]. Fractal growth of wax crystals can produce rough textures which give superhydrophobicity [39]. Recently, careful control of solvent and temperature during the drying process of polypropylene coatings has been shown to create surface textures suitable to exhibit superhydrophobicity [49].

### 3.2.2. Making Rough Structures Followed by Hydrophobic Treatments

Although starting with hydrophobic materials makes it easier to achieve superhydrophobicity, the hydrophobicity of the surface is not an absolutely necessary condition. Based on the Cassie–Baxter equation, it is also possible to produce a meta-stable superhydrophobic state with a material that has  $\theta_Y$  less than 90°. When certain micro-textures consisting of overhang structures with well-defined geometries are fabricated, superhydrophobicity can be attained with hydrogenterminated Si surfaces which have an intrinsic water contact angle of ~74° [50]. This is an example of precision surface engineering. A more widely used strategy is to roughen the material surface and then modify the surface chemistry with hydrophobic treatments. If the starting materials have intrinsic roughness, simple deposition of hydrophobic coatings can induce superhydrophobicity [37, 51].

Etching is an easy way to make rough surfaces. Polycrystalline metal surfaces can easily be roughened by chemical etching [52–54]. Like PTFE and polypropylene, many organic polymer surfaces and glass surfaces can be etched and roughened by plasma processes [55, 56]. On silicon surfaces, micrometer scale topographic structures such as grooves can be created with controlled width and depth with a high power pulsed laser beam [57]. After the roughening process, these sur-

faces can be treated with alkylsilane or fluorinated silane molecules to produce superhydrophobic properties.

Photo-lithography and electron beam lithography techniques developed in semiconductor processing have extensively been utilized to create periodic topographic patterns [58–60]. The use of lithographic patterning allows precise control of dimensions (width, height, and separation distances) and shapes (pillars *vs.* holes, facetted *vs.* rounded, continuous *vs.* discontinuous). The production of these controlled topographic features has played significant role in advancing fundamental understanding of the geometric effect on superhydrophobicity [21, 27, 61].

Another fast growing patterning technique in nanotechnology is nanosphere lithography. In this method, mono-dispersed polystyrene or silica nanoparticles are deposited in a close-packed lattice array by controlling the drying process of nanoparticle-containing solutions on flat substrate surfaces. Combined with proper surface modification chemistry, the ordered nanoparticle arrays produced in this method can generate superhydrophobic properties [62–64]. These nanoparticle arrays can also be used as a template to generate topographically textured patterns on substrate materials before hydrophobic modification of the surface [65].

Nanowires and nanotubes developed from recent drives in nanotechnology have extensively been used for preparation of superhydrophobic surfaces. There are many different types of nanowires and nanotubes that can be synthesized vertically on flat surfaces, forming pillars, through chemical vapor deposition methods. After the surface of these vertically oriented nanowires and nanotubes is made hydrophobic through a secondary chemical vapor deposition process, these materials render an excellent superhydrophobicity [66]. Anodization of aluminum can produce porous alumina membranes with controlled pore sizes and arrangements. After exposing to fluorinated silane, these membranes show an excellent superhydrophobicity [38]. The anodized alumina membrane can be used to impart vertically-oriented fibrillar topography to polymer surfaces making them superhydrophobic [67].

Another interesting approach is to deposit polymers and nanoparticles on substrate surfaces. One of the actively studied methods is to use a layer-by-layer (LbL) thin film deposition technique. In the LbL-deposition, alternatively charged polyelectrolytes or nanoparticles are deposited in sequence through electrostatic interactions and hydrogen bonding. By controlling particle size and number of deposition cycles, the film thickness and roughness can easily be controlled. After fluorination of the outmost layers, these films exhibit an excellent superhydrophobicity [68, 69]. Since the LbL deposition is conformal, this method can be applied to modify the surface of charged particles (silica, clays, etc.) of proper sizes using fluorinated polyelectrolytes [70]. Similarly, nanoparticles can be supported in certain block copolymer micelles and deposited to form porous films. Fluorination of these films with chemical vapor deposition produces superhydrophobic properties [71]. Electrochemical deposition of films is also a widely applied method in superhydrophobic surface fabrication. Through electroplating at underpotential or diffusion-limited conditions, metal films with proper surface roughness can be obtained. Fluorocarbon coatings on these rough surfaces give superhydrophobicity [72–74]. The LbL process can be used to produce superhydrophobicity on electrochemically deposited metal films [75–77]. In addition to metals, conducting polymers can also be produced with proper roughness to obtain superhydrophobicity [78, 79]. The growth of thin films containing rod-shaped crystals from a chemical bath has also been demonstrated for production of superhydrophobic substrates [80].

Another widely used approach in this area is a sol-gel process. In order to create surface roughness after deposition of thin films, a secondary component is included in the sol-gel deposition process which can be removed later by dissolution in hot water or sublimation. The removal of the secondary components gives porous structures. Subsequent fluorinated silane coating can render these sol-gel processed films superhydrophobic [81–83]. Microporous structures can be created through phase separation of organic polymer solutions and then used as a template for sol-gel processing of porous silica substrates. Fluorosilane treatment of these substrates produces superhydrophobic surfaces [84].

### 3.2.3. Depositing Hydrophobic Materials with Rough Textures

There are many processes reported in the literature that can simultaneously produce rough geometry and hydrophobic chemistry in a single step. For example, superhydrophobic foams with contact angles greater than 150° can be prepared directly from a sol–gel phase-separation process [85]. In this process, hydrophobicity has to be built into the organo-functionalized inorganic precursors and retained in the product by carefully controlling the sol–gel process conditions. Another phase-separation based approach is to grow a three-dimensional network of methylsiloxane cylindrical fibers [86]. This process produces a completely non-wetting surface with a water contact angle of 180°.

Plasma polymerization processes can be used to create fluorinated carbon films with a certain roughness. In this case, a precise control of plasma conditions as well as gas compositions is very critical to induce formation of plasma-dust particles in the gas phase so that the deposited films are rough enough to exhibit superhydrophobicity [36, 87, 88].

Electrospinning can create surface textures needed for superhydrophobicity. Electrospinning is a widely used technique to make ultra-thin polymer fibers. In this process, a polymer solution is charged in a capillary tube and electrically biased with respect to a grounded collector surface located  $\sim 10$  cm from the needle. The polymer solution is then ejected from the capillary into a jet form and the solvent evaporates leaving polymer fibers. By electrospinning polymers with hydrophobic properties, one can easily produce superhydrophobic fiber mats on the collector [89–92]. Of course, the electrospinning can also be used to make porous fiber mats

of any polymer or inorganic materials which can then be treated with hydrophobic surface modification methods to make them superhydrophobic [93, 94].

Certain inorganic materials can also be made into superhydrophobic surfaces. When ZnO and TiO<sub>2</sub> are produced into a thin film form consisting of vertically oriented nanorods, the low surface energy crystal planes are exposed at the film surface. These films show a good superhydrophobicity [95–97].

### 4. Summary and Outlook

In the past decade or so, we have seen renaissance of superhydrophobic research. One of the main driving forces in this recent interest is, in part, related to numerous potential practical applications of superhydrophobic surfaces and coatings. Various ways of fabricating superhydrophobic surfaces and coatings have been reported in the literature. So, it is now possible to choose the best method among several superhydrophobic treatment options which is suitable for target substrate materials — regardless of hydrophobicity and roughness of substrate surfaces. These methods range from simple physical roughening to highly engineered nanofabrication and surface modification. Some of the methods are applicable for continuous processing of various substrate materials.

However, there are still numerous issues that must be addressed for practical applications of superhydrophobic treatments. One of them is how to combine the superhydrophobicity with other desired surface or coating functions. For example, high transparency is an important property for many optical applications. While the surface roughness enhances the hydrophobicity, the scattering of light by rough surfaces decreases the transparency. Since the visible light wavelength is 400–750 nm, the surface roughness for transparent superhydrophobic films should be less than 100 nm. This has been addressed by many groups [81–83], but it does not meet the industrial need yet.

Another issue is the degradation of superhydrophobicity due to accumulation of stains over long periods of outdoor exposure. Inclusion of  $TiO_2$  can mitigate this problem through photocatalytic decomposition of deposits [98], but further improvement is needed in this area. In addition to water, oils can also be involved in various applications. In these cases, it would be desirable to have both superhydrophobicity and superoleophobicity. This is another active research area in this field [99, 100]. In some applications, surfaces responsive to external stimulations are highly attractive. There have been some successful examples of turning superhydrophobic surfaces to hydrophilic surfaces and *vice versa* using electrochemical redox reactions and photochemical reactions [79, 95–97, 101].

The most difficult challenge for practical applications of superhydrophobic surfaces would be mechanical durability. A needle-like or pillar-type structure is known to constitute an ideal geometry for superhydrophobicity [83], but this structure is generally not strong enough. Instead, a hemispherical or crater-like structure could be more desirable from a mechanical strength point of view [36, 84]. However, a fundamental question about how robust these surface textures can be remains to be addressed.

The advancement in synthetic superhydrophobic surface fabrication methods has provided an unprecedented level of control on the size and shape of micro- and nano-scale topographic structures, which has allowed extension of experimental studies on surface structure dependence of superhydrophobicity beyond the simple roughness scale [21, 27, 61]. The shape and connectivity of topographic features are important factors determining superhydrophobicity [11, 25]. In order to achieve high water contact angles (>150°), the surface roughness only at the annular boundary of the droplet may be enough [102, 103]. However, a topographic structure with proper roughness and shape throughout the entire droplet contact area is needed to attain a small sliding angle. Even in the simple roughness scale, a question of how rough is rough enough should be revisited since the superhydrophobicity has been observed for a surface with a root-mean-square roughness of ~15 nm, much smaller than typically expected [36]. These experimental results and observations invite more theoretical investigations on fundamentals of superhydrophobicity.

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### Ultra-hydrophobicity Through Stochastic Surface Roughness

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#### Abstract

The self-cleaning properties of ultra-hydrophobic surfaces are of great interest for technological applications. Specific surface roughness, essential for the dewetting effect, is not necessarily based on deterministic lotus leaf structures. Ultra-hydrophobicity also occurs on a large variety of stochastic, e.g., self-organized, roughness structures, which offers prospects for cost-effective manufacturing techniques (e.g., thin film deposition).

This work addresses the development of roughness design algorithms, which deliver application-focused structural parameters, required for efficient and targeted manufacturing processes. Our approach is based on the assessment of wetting-relevant surface structures by a specific roughness analysis using power spectral density functions. The resulting quantitative roughness criterion, a 'wetting parameter', enables the prediction of ultra-hydrophobicity for design purpose as well as for an efficient control and adoption of the manufacturing process. The reliability of this method is demonstrated for a variety of surfaces for engineering and optical applications.

For optical applications, the roughness design takes into account both wetting properties and optical quality (light scattering). Optical coatings manufactured according to the design specifications yielded low-scattering, ultra-hydrophobic surfaces.

#### Keywords

Ultra-hydrophobicity, lotus effect, wetting, roughness, optical coating, self-organizing nanostructures

### 1. Introduction

The wetting behavior of a large variety of surfaces is of crucial importance for their key applications. These applications extend from consumer products such as architectural glass, automotive mirrors and eye glasses where cleaning aspects play a dominant role, to engineering components like steel surfaces with critical lubrication properties, fluid repellence of medical instruments, to ultra-precision optics designed for operation in immersion fluids. Ultra-hydrophobicity has proved as a

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major route to realize self-cleaning surfaces, and this property has been shown to be based on two essential aspects: the intrinsic material properties and a rough surface structure. Smooth surfaces with appropriate molecular structures exhibit an 'intrinsic hydrophobicity' with water contact angles up to 120°. Ultra-hydrophobicity with considerably higher water contact angles can only be achieved through an additional rough surface structure [1]. This structural aspect, in particular regarding stochastic surface roughness, will be addressed in this paper.

Nature provides impressive examples of how rough structures make a surface ultra-hydrophobic and hence self-cleaning. In particular, the so-called lotus effect has become popular: water drops entirely roll off the lotus leaf and drag along any dirt particles without leaving residues [2]. The SEM images in Fig. 1 display the pronounced structural features. Consequently, the search for a technological realization of ultra-hydrophobic surfaces was initially focused on similar, regular structures which are known to exist in the flora and fauna. However, a thorough examination of the surfaces of other plant leaves, such as *Brassica oleracea var. gongylodes*, reveals that ultra-hydrophobicity also occurs on completely different and irregular structures (Fig. 2). With the possibility of ultra-hydrophobicity based on irregular stochastic structures, attractive potentials for the technological realization of such surfaces arise together with the employment of various fabrication processes. Up to now, the generation of ultra-hydrophobic surfaces, based on non-deterministic, stochastic roughness structures has mainly relied on trial and error principles.

Therefore, general and quantitative criteria have to be established which define stochastic roughness structures that turn an (intrinsically hydrophobic) surface into an ultra-hydrophobic one.

Furthermore, in the case of optical applications, there is another requirement to be fulfilled by the roughness structures in addition to the desired wetting properties:



Figure 1. SEM images of roughness structure on a lotus leaf (Nelumbo nucifera).



Figure 2. SEM images of roughness structure on a kohlrabi leaf (Brassica oleracea var. gongylodes).

the light scattering losses induced by enhanced surface roughness must not reduce the optical quality.

### 2. Modelling Procedures

The knowledge of the functional relationship between surface roughness and wetting properties constitutes the key to the design and hence efficient technological realization of ultra-hydrophobic surfaces. Quantitative criteria of surface roughness characteristics, essential for ultra-hydrophobicity, have so far been established only for model surfaces (e.g., sinusoidal or crenelated surfaces [3, 4]). In the following section, we report on our approach to derive a universal quantitative criterion for stochastic roughness structures, which turn intrinsically hydrophobic surfaces into ultra-hydrophobic surfaces.

### 2.1. Structural Criterion for Ultra-hydrophobicity of Stochastic Rough Surfaces

The construction principle of ultra-hydrophobic surfaces is based on a combination of hydrophobic (intrinsic) material properties and appropriate surface roughness structures. The wetting of liquids on rough hydrophobic surfaces can occur in two different equilibrium states, depending on the specific roughness characteristics [5]. In the case of homogeneous wetting the liquid penetrates into roughness grooves (Fig. 3, left), while in heterogeneous wetting, air cavities are entrapped between the liquid and the solid (Fig. 3, right).

The wetting of a liquid drop on a solid surface can be quantified by the apparent contact angle (CA)  $\Theta_{ap}$ . The contact angle  $\Theta_{ap}$  is defined as the angle between the tangent to the liquid–gas interface and the geometrical shape of the solid–liquid interface at the contact line between the three phases, as shown in Fig. 3. While on ideal surfaces (no roughness, chemically homogeneous) only one thermodynamically stable contact angle (intrinsic Young-CA  $\Theta_Y$ ) exists, wetting on



Figure 3. Homogeneous (left) and heterogeneous (right) wetting on a rough surface.

rough surfaces is characterized by a contact angle spectrum [6]. The multiplicity of metastable contact angles within the spectrum is related to the local variation of the topographic slope.

The highest and lowest values within the spectrum are called advancing contact angle  $\Theta_A$  and receding contact angle  $\Theta_R$ , respectively. The methods employed for appropriate contact angle measurement are described below in Section 3.2.

The width of the CA spectrum, called contact angle hysteresis, is closely related to the minimum tilting angle  $\alpha$  of the surface, at which a drop starts sliding or rolling off. The condition for a liquid drop of surface tension  $\sigma_{LV}$  to start moving over the tilted surface is given by the minimum force acting per unit length of the drop perimeter [7]:

$$f_{\rm line} = \frac{\sigma_{\rm LV}(\cos\Theta_{\rm R} - \cos\Theta_{\rm A})}{2}.$$
 (1)

A universal definition of ultra-hydrophobic surfaces is given by the following two criteria:

- high apparent contact angle  $\Theta_{ap} > 150^{\circ}$  (Note that the value of  $\Theta_{ap}$  related to ultra-hydrophobicity is not exactly defined.),
- low contact angle hysteresis and related low roll-off angle  $\alpha$ .

To comply with both criteria, wetting has to occur necessarily in the heterogeneous wetting state [8].

For wetting on rough surfaces the fundamental relationships between the intrinsic Young-CA  $\Theta_{\rm Y}$  and the most stable CA within the CA spectrum (global minimum in the Gibbs energy of the wetting system) were given by Wenzel [9] and Cassie and Baxter (CB) [10].

The Wenzel contact angle  $\Theta_W$  in the case of homogeneous wetting is related to  $\Theta_Y$  by means of the roughness ratio r, which is defined as the ratio of the true solid surface area to its projected area:

$$\cos(\Theta_{\rm W}) = r \cos(\Theta_{\rm Y}). \tag{2}$$

The CB contact angle  $\Theta_{CB}$  which describes the most stable contact angle in the case of heterogeneous wetting is given by:

$$\cos(\Theta_{\rm CB}) = r_f f \cos(\Theta_{\rm Y}) + f - 1, \tag{3}$$

with the fraction f of the projected surface area that is wetted by the liquid and the roughness ratio  $r_f$  of the wetted area.

The application of these equations for the design of surface roughness structures and the prediction of their wetting properties has so far been limited to deterministic model surfaces. For complex stochastic surface structures, the thermodynamic analysis (analytical and numerical) of the transition conditions (homogeneous  $\rightarrow$ heterogeneous wetting) cannot be accomplished. The same applies for the theoretical and experimental determination of the parameters f and  $r_f$  in case of heterogeneous wetting. Even the roughness ratio r of a homogeneous wetting system is experimentally inaccessible due to the spatial-frequency bandwidth limitation of roughness measurement techniques determined by scan length and sampling distance.

Our approach to derive a quantitative criterion for the roughness characteristics of ultra-hydrophobic surfaces with stochastic roughness properties is based on roughness analysis by power spectral density (PSD) functions and subsequent data reduction algorithm [11].

The PSD, which provides the relative strength of roughness components as a function of spatial frequency, can be calculated from topographic surface data [12] as:

$$PSD(\mathbf{f}) = \lim_{A \to \infty} \frac{1}{A} \left| \int_{\mathbf{A}} z(\mathbf{r}) \exp(-2\pi i \mathbf{f} \cdot \mathbf{r}) \, \mathrm{d}\mathbf{r} \right|^2, \tag{4}$$

where  $z(\mathbf{r})$  represents the height data of the roughness profile,  $\mathbf{r}$  the position vector, and  $\mathbf{f}$  the spatial frequency vector in the x-y plane. A denotes the surface area of the measuring field  $\mathbf{A}$ . In the case of isotropic surfaces PSD( $\mathbf{f}$ ) becomes independent of the surface direction of the spatial frequency vector. Unlike simple roughness parameters (e.g., rms roughness) the PSD considers both the vertical and lateral dimensions of roughness components.

Our approach is based on the findings of Johnson and Dettre [3], that for sinusoidal hydrophobic surfaces the most stable contact angle as well as the transition from homogeneous to heterogeneous wetting state depend on their roughness ratio r, but not on their absolute magnitude. Since stochastic surface roughness can be composed as a spectral superimposition of sinusoidal roughness components, we derived a novel quantity from the PSD, which we called the wetting parameter  $\kappa_B$ . In the following, a short overview of the algorithm yielding  $\kappa_B$  is given:

- 1. Transformation of the PSD(f) into the amplitude spectrum A(f).
- 2. Calculation of  $A(f) \cdot f$ , which denotes the spectrum of the aspect ratio between the amplitude and the spatial wavelength  $\lambda_s$  ( $\lambda_s = 1/f$ ) of sinusoidal roughness components, which is related to the roughness ratio *r*.
- 3. Integration of the  $A(f) \cdot f$  spectrum over the logarithmic spatial frequency range.

The wetting parameter  $\kappa_B$  is a scale invariant parameter corresponding to the independence of the wetting properties of sinusoidal surfaces structure from their absolute magnitude. Similar wetting properties can be achieved by significantly different structure sizes, as long as their typical dimensions are very small compared with the size of the drop. In practice, this is demonstrated by the diversity of natural and artificial ultra-hydrophobic surfaces which rely on both nanometer- and micrometer-sized roughness features [2, 13, 14].

By experimental investigations of sample series covering a large variety of roughness characteristics, but with the same hydrophobic material properties (all samples were coated with a thin RF sputtered Au layer and a molecular decanethiol film to obtain intrinsic CA about 110°), empirical correlation between  $\kappa_B$  and the apparent CA was established (Fig. 4). Consequently, the wetting parameter is capable of describing the relationship between the roughness and wetting properties of stochastic rough surfaces, separated from the intrinsic material effect (intrinsic CA  $\Theta_Y$ ). As the diagram reveals, high apparent contact angles  $\Theta_{ap} > 150^\circ$ , as necessary for ultra-hydrophobicity, were observed for values of  $\kappa_B \approx 0.4$  or higher. It should be emphasized that high apparent contact angles constitute an essential but not a sufficient criterion for ultra-hydrophobicity. Accordingly, we defined this threshold as a general quantitative criterion describing which roughness properties a surface has necessarily to fulfill in order to become ultra-hydrophobic.

Design and assessment of wetting-relevant stochastic surface roughness by means of  $\kappa_B$  constitute the key to an efficient and targeted technological realization, in contrast to conventional trial and error methods. For this purpose we developed



**Figure 4.** Experimentally obtained relationship between the wetting parameter  $\kappa_B$  and the (apparent) water contact angle. The measurements refer to a number of different types of rough surfaces with same hydrophobic material properties (all samples were coated with a thin RF sputtered Au layer and a molecular decanethiol film to obtain intrinsic CA about 110°).

roughness design algorithms in order to provide application-focused structural parameters required for manufacturing processes.

Furthermore, the wetting parameter also provides benefit for the control and adoption of the manufacturing process by characterization of the wetting effect of the fabricated roughness structures, independent of their hydrophobic material properties. Roughness characterization enables the prediction of potential wetting properties without the need for laborious chemical surface modification and subsequent wetting measurements for samples with  $\kappa_B$  significantly below 0.4. However, the verification of potentially qualified surfaces ( $\kappa_B \approx 0.4$  or higher) in terms of ultra-hydrophobicity requires final examination of wetting properties.

### 2.2. Design of Ultra-hydrophobic Surfaces

The roughness design can be performed by 'virtual' alteration of the surface roughness properties, approximated by analytical model PSD functions. Several PSD models exist for the description of surface roughness characteristics [15]. The fractal model, for example, is applied if roughness characteristics are assumed to be self-affine:

$$PSD_{\text{fractal}}(f; K, n) = \frac{K}{f^{n+1}}.$$
(5)

The parameters K and n are related to the vertical and fractal dimensions of the self-affine roughness components, respectively. Surfaces roughness features with characteristic mean vertical and lateral dimensions can be described using the ABC model:

$$PSD_{ABC}(f; A, B, C) = \frac{A}{(1 + B^2 f^2)^{(C+1)/2}}.$$
(6)

From the three parameters A, B and C, the rms roughness  $\sigma$  and correlation length  $\tau$  can be derived. The roughness characteristics of a large variety of real surfaces can be approximated either by a single kind of PSD model or by their combinations. Typical PSD curves for the fractal and ABC model under variation of parameters are shown schematically in Fig. 5.



Figure 5. PSD model functions with varied parameters: ABC model (left) and fractal model (right).

By varying the model parameters within reasonable limits we searched for parameter sets that met the above defined  $\kappa_B$  threshold criterion for ultrahydrophobicity. In the case of the ABC model, parameter variation corresponds to a modification of the mean vertical and lateral dimensions of the characteristic roughness features.

Specific results of calculated  $\kappa_B$  values for a diversity of ABC model functions are shown in Fig. 6. The model parameters *A* and *B* were varied within defined bandwidths (parameter *C* fixed at a value of 2.5) and translated into equivalent parameters  $\sigma \cdot \tau$  and  $\tau$ . The mean vertical and lateral dimensions of the described roughness features are in the nanometer range. They can, however, be generally extended into the micrometer range as well, as the diagram expresses the independence of  $\kappa_B$  on the absolute structural dimension.

Structural parameters  $\sigma$  and  $\tau$  of PSD solutions with  $\kappa_B \approx 0.4$  (or higher) define the requirements for the manufacturing process. From the technological point of view it can be mentioned: The higher the aspect ratio of roughness structures, which is preferred in the sense of ultra-hydrophobic wetting properties (high  $\kappa_B$  value), the higher the limitation of potentially qualified manufacturing processes.

In addition to the desired wetting properties, another requirement arises when optical applications are addressed: light scattering losses induced by the enhanced surface roughness have to be controlled and kept to a certain limit. The scatter level must remain below an application-dependent threshold in order to maintain optical quality. The limit varies according to the specific optical application. For architectural glass application, for instance, the light scattering must not dis-



Figure 6. Calculated values of wetting parameter  $\kappa_B$  for a diversity of ABC model functions.

turb the optically esthetic appearance. The corresponding threshold was found by experiments that linked visual inspection with quantitative scatter measurements [16]. Under specific conditions for test sample observation (dark background, no ambient light) thresholds for total scattering (TS, according to ISO 13696) at  $\lambda = 514$  nm in the forward and backward scatter directions were determined as:  $TS_f = (2.2 \pm 0.3) \times 10^{-3}$  and  $TS_b = (1.7 \pm 0.2) \times 10^{-3}$ .

Ultra-hydrophobicity and low light scatter losses are opposite properties in principle, as surface roughness always acts as a scatter source. The ultra-hydrophobicity of optical surfaces is necessarily based on nanometer-sized roughness structures in order to maintain optical quality (low scatter losses). Different approaches are possible to realize appropriate roughness structures on glass substrates: substrate roughening (e.g., by etching processes), deposition of coatings with self-organizing nano-roughness (e.g., by vacuum process or wet-chemical technique) or combination of both processes. Subsequent chemical surface treatment (hydrophobic top layer) is necessary in order to provide the necessary intrinsic hydrophobicity (Fig. 7).

Several research groups have reported on the fabrication of optically transparent ultra-hydrophobic surfaces by coatings (e.g., silica-based sol–gel-films [17], boehmite films [18]) or surface treatments (e.g., plasma etching [19]). These realization processes were, however, not systematically directed by design targets which consider surface roughness in terms of both wetting and light scattering properties.

Appropriate roughness design is again a key to enhance the promising potential of common coating/surface treatment techniques for the generation of nanostructured ultra-hydrophobic, low-scatter surfaces. For this purpose, we extended our nanostructure-design algorithm for providing application-focused structural parameters for both optimum wetting properties and optical quality. The design procedures developed are not only suitable for single interfaces but have also been tailored for surfaces with multilayer coatings.

For keeping the optical losses at a controllably low level — as a result of the nano-dimensions — we benefit from another attractive property of the PSD functions: their close connection to optical scattering. For coated surfaces, the approximation for the overall surface roughness characteristics is described by multiple components: the PSDs of the thin film layers (ABC model) and the PSD of the pure substrate (measured values or fractal model). This enables a separate treatment of



**Figure 7.** Realization of ultra-hydrophobic optical surfaces by coating deposition on glass substrates (schematically).

each roughness contribution. The light scattering (in transmission and reflection directions) of the system, with defined surface/interface PSDs and optical properties (refraction indices, layer thickness), can be predicted using a multilayer vector scattering program [20].

Design solutions are given by the subset of structural parameters that meet both criteria:  $\kappa_B \approx 0.4$  (or higher) for ultra-hydrophobicity and TS < applicationdependent threshold for optical quality. In principle, the level of light scattering exhibits proportional dependence on the structural parameter  $\sigma \cdot \tau$ . Accordingly the solution subset (e.g., Fig. 6) is limited towards high values of  $\sigma \cdot \tau$ , depending on the specific optical design properties and scatter threshold.

### 3. Characterization Procedures

### 3.1. Roughness Measurement and Analysis

The wetting properties of surfaces can be potentially affected by roughness structures with lateral extensions ranging from the sub-millimeter scale down to the nanometer scale. The assessment of wetting-relevant roughness components, therefore, requires surface topography characterization within the corresponding spatial frequency range  $f = (10^{-3}, ..., 10^3) \, \mu m^{-1}$ .

In addition, the analysis of roughness components inducing light scattering (in the visible spectrum) of optical surfaces is focused on the mid-spatial frequency range  $f = (5 \times 10^{-2}, ..., 2) \, \mu m^{-1}$ .

For capturing roughness component within the high- and mid-spatial frequency ranges  $f = (5 \times 10^{-2}, ..., 10^3) \,\mu\text{m}^{-1}$  we used atomic force microscopy (AFM) at various scan ranges from  $200 \times 200 \,\text{nm}^2$  to  $50 \times 50 \,\mu\text{m}^2$ . Micrometer-sized roughness components within the low spatial frequency range  $f = (10^{-3}, ..., 1) \,\mu\text{m}^{-1}$  were measured by confocal laser scanning microscopy (LSM) within scan ranges  $92 \times 92 \,\mu\text{m}^2$  to  $1.8 \times 1.8 \,\text{mm}^2$ .

From digital topographic surface data z(m, n) within a certain scan range  $L(M \times M$  measurement points) the two-dimensional PSD function was calculated:

$$PSD(f_x, f_y) = \frac{1}{L^2} \left| \sum_{m,n=1}^{M} z(m,n) e^{-i2\pi\Delta L(mf_x + nf_y)} (\Delta L)^2 \right|^2.$$
(7)

As isotropic roughness is considered, the isotropic PSD(f) was calculated after transformation into polar coordinates and averaging over all surface directions (polar angles  $\varphi$ ):

$$PSD(f) = \frac{1}{2\pi} \int_0^{2\pi} PSD(f,\varphi) \,\mathrm{d}\varphi.$$
(8)

The single bandwidth-limited PSDs of a certain sample, derived from various measurements in different scan ranges, were combined to a unique Master-PSD [21].

PSD results from AFM measurements in the high spatial frequency range  $f = (10, ..., 10^3) \ \mu m^{-1}$  (lateral dimensions: 100 nm, ..., 1 nm) can be significantly

modified by distortion of the measured surface profile due to the non-vanishing tip size (radius of the apex 10 nm). In order to study the content of available roughness information in this critical range we performed systematic experimental/empirical work [22]. It turned out that unavoidable tip size effects mainly underestimated the PSD values toward higher spatial frequencies. In spite of significant modification of the absolute PSD values, the content of available topographic information turned out to be sufficiently high for comparing different samples.

### 3.2. Contact Angle Measurement

For the characterization of wetting properties we employed dynamic contact angle measurements as well as measurements of sliding/roll-off angles using a Data-Physics OCA20 measurement system.

Dynamic contact angle measurements were performed for the determination of the highest and lowest values within the range of metastable contact angles of a real wetting system [6]. During the measurement process, the volume of the sessile drop was varied over time using the needle-in-drop method. During the increase of the drop volume (typically: initial volume of 10 µl increased to 60 µl) the contact line is initially pinned while the CA is increasing (stage 1 in Fig. 8). After reaching a maximum value (advancing contact angle  $\Theta_A$ ), the contact line advances over the surface (stage 2 in Fig. 8). Similarly, the reduction of drop volume (typically: volume of 60 µl decreased to 10 µl) causes an initial pinning of the contact line while the CA is decreasing (stage 3 in Fig. 8). After reaching a minimum value (receding contact angle  $\Theta_R$ ), the contact line recedes at further volume reduction (stage 4 in Fig. 8).



**Figure 8.** Typical stages of drop shape development (schematically) during dynamic contact angle measurement cycle (after [6]). The increase or decrease of drop volume is indicated by arrows.

The measurement of sliding angles and roll-off angles at a defined drop volume of  $35 \ \mu$ l was performed by motorized rotation of the contact angle measurement system along its horizontal axis.

### 4. Results and Discussion

We have analyzed the roughness of a variety of natural and artificial surfaces in terms of the wetting parameter  $\kappa_B$  to evaluate their potential for ultra-hydrophobicity. The predictions 'ultra-hydrophobic' or 'not ultra-hydrophobic' based on  $\kappa_B$  were followed by dynamic contact angle measurements and sliding/roll-off angle measurements. All samples exhibited comparable hydrophobic material properties with intrinsic contact angles in the range  $\Theta_{\rm Y} = 100^\circ, \ldots, 120^\circ$ . Intrinsic contact angles were estimated from static contact angle measurements on smooth glass substrates or silicon wafers (rms roughness < 0.5 nm) coated with hydrophobic top layers.

### 4.1. Plant Leaves

The topographies of natural ultra-hydrophobic surfaces, such as several plant leaves, are composed of roughness structures with micrometer and nanometer dimensions. For the examples of two representative plant leaves, the well-known lotus (*Nelumbo nucifera*) and the kohlrabi (*Brassica oleracea var. gongylodes*), we investigated the contributions from differently sized roughness components to the dewetting properties. The characterization of wetting properties by roll-off angle measurements (drop volume:  $35 \ \mu$ l) yielded extremely low values of 2.5° and 5.5° for the lotus and kohlrabi leaves, respectively. These roll-off angle values constitute references for the assessment of artificial ultra-hydrophobic surfaces.

The wetting-relevant roughness components were captured by LSM measurements. AFM measurements within the high spatial frequency range proved to be not feasible due to the extended vertical dimension of the roughness structures. Qualitative comparison of the surface topographies exhibited significantly different micrometer-sized roughness structures (Fig. 9).

The comparison of the corresponding Master-PSD curves is given in Fig. 10. The characteristic cellular structures of the leaf surfaces occur as characteristic 'bumps' at low spatial frequencies in the otherwise fractal-like PSDs. Within the spatial frequency range  $f = (10^{-3}, ..., 1) \, \mu m^{-1}$ ,  $\kappa_B$  values of 0.2 and 0.4 were calculated for the kohlrabi and the lotus leaves, respectively. In comparison, very high  $\kappa_B$  values > 1.0 (lotus: 2.1; kohlrabi: 1.5) were estimated for both samples within the spatial frequency range  $f = (1, ..., 10) \, \mu m^{-1}$  after extrapolation of the PSD curves. This means the expected ultra-hydrophobicity of these leaves is mainly supported by sub-micrometer roughness components, even in the case of the famous micrometer-sized 'regular' surface structures of the lotus leaf.



**Figure 9.** LSM topography images of ultra-hydrophobic plant leaves: kohlrabi (left) and lotus (right); scan size:  $460 \times 460 \ \mu\text{m}^2$  (top) and  $92 \times 92 \ \mu\text{m}^2$  (bottom).



Figure 10. Comparison of master PSD curves for kohlrabi and lotus leaves.

### 4.2. Microrough Engineered Surfaces

The following examples show results obtained on laser-structured steel surfaces, manufactured under variation of processing parameters, with hydrophobic top lay-



**Figure 11.** Laser-structured ultra-hydrophobic steel surface (sample A); left: LSM measurement  $(460 \times 460 \ \mu\text{m}^2)$ ; right: AFM measurement  $(1 \times 1 \ \mu\text{m}^2)$ .



**Figure 12.** Dynamic contact angle measurement on laser-structured ultra-hydrophobic steel surface (sample A); left: advancing contact angle; right: receding contact angle.

ers (fluorine-doped diamond-like carbon films; manufactured by the Fraunhofer Institute IWS, Dresden, Germany) [23]. The analysis of the micrometer- and nanometer-sized roughness components of sample A (Fig. 11) yielded a  $\kappa_B$  value of 0.50. Consequently, ultra-hydrophobicity was predicted. The subsequent wetting measurement confirmed this result: Advancing and receding contact angles of 157° and >140° (Fig. 12), respectively, and a roll-off angle < 10° were measured. In comparison, a  $\kappa_B$  value of 0.14 predicted non-ultra-hydrophobicity for sample B (Fig. 13) which was in agreement with measured high contact angle hysteresis (Fig. 14).

### 4.3. Nanorough Optical Surfaces

The ultra-hydrophobicity of optical surfaces is necessarily based on nanometersized roughness structures in order to maintain optical quality (low scatter losses). Systematic roughness design in terms of the parameter  $\kappa_B$  constitutes a key to a cost-effective manufacturing process. As stochastic structures have proved suitable for the desired ultra-hydrophobic effect, in principle a large range of potential manufacturing techniques can be considered. In particular, plasma processes, like etching techniques, and coating processes such as magnetron sputtering and sol–gel



**Figure 13.** Laser-structured hydrophobic steel surface (sample B); left: LSM measurement  $(460 \times 460 \ \mu\text{m}^2)$ ; right: AFM measurement  $(1 \times 1 \ \mu\text{m}^2)$ .



**Figure 14.** Dynamic contact angle measurement on laser-structured hydrophobic steel surface (sample B); left: advancing contact angle; right: receding contact angle.

processes can be used to produce self-organizing rough structures through appropriate process specifics. In the following, examples of realization by coating processes are presented. The surface chemistry of all samples was modified by a molecular hydrophobic top layer (fluoroalkylsilane) in order to deliver intrinsic hydrophobicity.

### 4.3.1. Sputtered Oxide Coatings

ZrO<sub>2</sub> single layer coatings of different roughness properties were deposited by magnetron sputtering under varying deposition conditions (manufactured by K. Reihs, SuNyx, Leverkusen, Germany). AFM measurement results for the examples of two different coatings are shown in Fig. 15. The rms roughness values  $(1 \times 1 \ \mu m^2)$  of samples A and B were 3 nm and 9 nm, respectively. PSD analysis within the wetting-relevant spatial frequency range  $f = (1, ..., 10^3) \ \mu m^{-1}$  revealed  $\kappa_B$  values significantly below 0.4 (sample A: 0.11; sample B: 0.22) which predicted non-ultra-hydrophobic properties. Dynamic contact angle measurements, performed to confirm the prediction, observed an insufficient advancing contact angle of 127° for sample A. In the case of sample B the advancing contact angle of 147° was promising, but the high contact angle hysteresis > 70° (receding contact angle = 75°) was characteristic for the homogeneous, non-ultra-hydrophobic wetting state. In both



**Figure 15.** AFM topography images  $(1 \times 1 \ \mu m^2)$  of ZrO<sub>2</sub> single layer coatings of different roughness properties; left: sample A; right: sample B.



**Figure 16.** AFM topography image  $(1 \times 1 \ \mu m^2)$  of an ultra-hydrophobic Al<sub>2</sub>O<sub>3</sub> single layer coating, deposited by magnetron sputtering.

cases the aspect ratios of the roughness structures were insufficient to satisfy the design specifications.

Coatings with surface structures in accordance with the design specifications were achieved by deposition of magnetron sputtered  $Al_2O_3$  single layer coatings (manufactured by K. Reihs, SuNyx, Leverkusen, Germany). The surface structures showed significantly different characteristics (Fig. 16) compared to ZrO<sub>2</sub> coatings and an even higher rms roughness of 14 nm (1 × 1  $\mu$ m<sup>2</sup>).

The  $\kappa_B$  value of 0.39 indicated reasonable compliance with the essential requirement for ultra-hydrophobicity ( $\kappa_B \approx 0.4$  or higher). This prediction was later confirmed by the measurement of high advancing and receding contact angles of 156° and 120°, respectively. The low contact angle hysteresis < 40° was in accordance with a low roll-off angle of 23° (drop volume: 35 µl). Moreover, the optical scatter losses of TS = 0.04% remained clearly beneath the scatter limit value defined for architectural glass application.

Figure 17 displays a spherical water drop rolling off a glass slide coated with a rough  $Al_2O_3$  layer plus a molecular hydrophobic top layer. The drop removes artificial contaminants (graphite powder) on its track.



**Figure 17.** Water drop (volume:  $\approx 50 \ \mu$ l) rolling off an ultra-hydrophobic Al<sub>2</sub>O<sub>3</sub> single layer coating (with hydrophobic top layer), removing artificial contaminants.



**Figure 18.** AFM topography image  $(1 \times 1 \ \mu m^2)$  of an ultra-hydrophobic Al<sub>2</sub>O<sub>3</sub> single layer coating, deposited by sol–gel process.

### 4.3.2. Sol–Gel Coatings

Coatings of Al<sub>2</sub>O<sub>3</sub> single layers were also deposited by a wet-chemical sol–gel process (manufactured by M. Mitterhuber, ETC Products, Deggendorf, Germany). The surface structures shown in Fig. 18 turned out to be qualitatively similar to the sputtered species, but exhibit even higher rms roughness values of 28 nm  $(1 \times 1 \ \mu m^2)$  as well as higher aspect ratios. Pronounced ultra-hydrophobic properties were predicted by a high  $\kappa_B$  value of 0.81. This was confirmed by measured high advancing and receding contact angles of 154° and 142°, respectively. Roll-off angle measurements yielded very small values < 10° (drop volume: 35  $\mu$ l) according to the low contact angle hysteresis < 15°. In addition to the excellent wetting properties, optical scatter losses of TS = 0.06% (transmission direction) remained well below the defined acceptance threshold for architectural glass application.

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**Figure 19.** Comparison of master PSD curves for optical coatings: non-ultra-hydrophobic ZrO<sub>2</sub> single layers and ultra-hydrophobic Al<sub>2</sub>O<sub>3</sub> single layers.



**Figure 20.** Comparison of wetting parameter  $\kappa_B$  within specific spatial frequency decades for ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> single layer coatings.

For comparison of the roughness characteristics of all mentioned nanorough optical surfaces the corresponding Master-PSD curves are shown in Fig. 19. It is obvious that the typical shape of the thin film PSDs can be well approximated by ABC model functions within the scope of the design process (Fig. 5, left).

Values of the wetting parameter  $\kappa_B$ , calculated for specific spatial frequency decades within the range  $f = (10^{-1}, ..., 10^3) \,\mu\text{m}^{-1}$  are given in Fig. 20. Obviously, only roughness components at spatial frequencies above  $f = 1 \,\mu\text{m}^{-1}$ , which means structured components with nanometer dimensions, are relevant for

the wetting properties. Furthermore, it is interesting that roughness contributions continuously rise with increasing spatial frequency, in spite of the pronounced underestimation of PSD values due to AFM tip size effects.

### 5. Summary

The ultra-hydrophobic effect of functional surfaces can be achieved by a variety of entirely different surface structures. Neither specific regular structures nor uniform structure sizes are necessary. Stochastic surface roughness is suited as well. This opens up attractive potential for a wide range of technological processes for the realization of ultra-hydrophobic surfaces such as self-organizing nanostructuring during thin film deposition, plasma etching and wet chemical procedures.

An important key to an efficient technological realization consists in the design and assessment of the wetting-relevant stochastic roughness structures. For this purpose, we developed roughness design algorithms which provide optimum structural parameters for each specific application. On this basis, the most appropriate manufacturing technique can be selected and optimized.

Our approach to the assessment of wetting-relevant surface structures utilizes a novel roughness analysis procedure based on power spectral density functions. This finally results in a universal 'wetting parameter'  $\kappa_B$  which constitutes a reliable indicator for stochastic surface structures essentially required to create ultrahydrophobicity. The parameter  $\kappa_B$  can support the manufacturing process (e.g., thin film deposition) in a twofold way: First, it defines the appropriate roughness in the design process in contrast to conventional trial and error approaches. Second, it enables separate control and characterization of the wetting effect of the fabricated roughness structures, independent of the hydrophobic material properties. So far, any judgment about the potential of stochastic roughness structures to generate ultra-hydrophobicity has required contact angle measurement, which does not yield a distinction between structural and material effects.

Examples were given for microrough laser-structured surfaces as well as for selforganized nanorough optical coatings.

Future investigations will be directed to the investigation of potential correlation between  $\kappa_B$  and roughness-induced superhydrophilicity. We expect from the theory that our approach should work in a similar way for the hydrophilic domain as for the hydrophobic domain.

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