Mechanically Durable Superhydrophobic Surfaces

Tuukka Verho, Chris Bower, Piers Andrew, Sami Franssila, Olli Ikkala, and Robin H. A. Ras*

Development of durable non-wetting surfaces is hindered by the fragility of the microscopic roughness features that are necessary for superhydrophobicity. Mechanical wear on superhydrophobic surfaces usually shows as increased sticking of water, leading to loss of non-wettability. Increased wear resistance has been demonstrated by exploiting hierarchical roughness where nanoscale roughness is protected to some degree by large scale features, and avoiding the use of hydrophilic bulk materials is shown to help prevent the formation of hydrophilic defects as a result of wear. Additionally, self-healing hydrophobic layers and roughness patterns have been suggested and demonstrated. Nevertheless, mechanical contact not only causes damage to roughness patterns but also surface contamination, which shortens the lifetime of superhydrophobic surfaces in spite of the self-cleaning effect. The use of photocatalytic effect and reduced electric resistance have been suggested to prevent the accumulation of surface contaminants. Resistance to organic contaminants is more challenging, however, oleophobic surface patterns which are non-wetting to organic liquids have been demonstrated. While the fragility of superhydrophobic surfaces currently limits their applicability, development of mechanically durable surfaces will enable a wide range of new applications in the future.

1. Introduction

A myriad of reports have been published on ways to fabricate superhydrophobic non-wetting surfaces.[1–7] These surfaces, which possess the virtue of having a very large water contact angle and exhibiting little sticking to water drops, have numerous applications in self-cleaning paints and windows,[8] non-wetting fabrics,[9–12] anti-fogging,[13] anti-icing,[14] buoyancy[15] and flow enhancement[16] to name a few. However, the practicality of non-wetting surfaces is hampered by
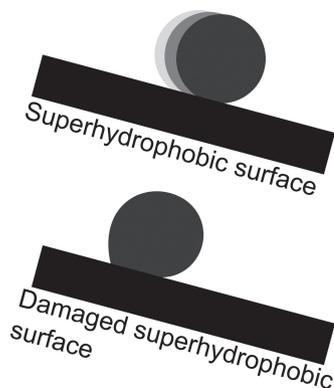
T. Verho, Prof. O. Ikkala, Dr. R. H. A. Ras
Molecular Materials
Department of Applied Physics
Helsinki University of Technology/Aalto University
Puumiehenkuja 2, FI-00076 Aalto, Espoo, Finland
E-mail: robin.ras@tkk.fi

Dr. C. Bower, Dr. P. Andrew
Nokia Research Center
Broers Building (East Forum)
21 JJ Thomson Avenue, Madingley Road
Cambridge CB3 0FA, UK

Prof. S. Franssila
Department of Materials Science and Engineering
Helsinki University of Technology/Aalto University
Vuorimiehentie 2, FI-00076 Aalto, Espoo, Finland

the poor mechanical stability of the microscopic surface topography that is essential for very large contact angles. Despite the importance of mechanical durability in applications, this aspect has received relatively little attention until very recently. Furthermore, mechanical contact may also leave impurities on non-wetting surfaces, causing a decline in their properties. Here, we present a short overview of the recent advances in developing mechanically resilient superhydrophobic surfaces and review the approaches that can be taken to avoid degradation due to contamination.

Usually, two criteria are applied in defining superhydrophobicity. First, the equilibrium water contact angle θ of a superhydrophobic surface must be larger than 150°. Second, water must not stick to the surface, i.e. droplets must roll off easily. The second condition is related to the contact angle hysteresis $\Delta\theta$ of the surface — the difference between the largest (advancing) and smallest (receding) stable contact angle $\theta_{adv} - \theta_{rec}$. The maximum lateral force F_{lat} that a distorted droplet can build up depends on θ_{adv} and θ_{rec} as[17]

$$F_{lat} \propto \cos\theta_{rec} - \cos\theta_{adv} \qquad (1)$$

which can be approximated for small hysteresis as $F_{lat} \propto \Delta\theta \sin\theta$. In many cases, damage and contamination do not dramatically decrease the equilibrium contact angle θ of a non-wetting surface (or the measured 'static' contact angle) but do decrease the receding angle θ_{rec} and so cause a large hysteresis, affecting the rolling behavior of water droplets due to a larger F_{lat} (**Figure 1**).

Smooth surfaces can have an intrinsic contact angle only up to about 120°.[18,19] Superhydrophobicity — angles over 150° — can be achieved by roughening a hydrophobic surface to establish a stable Cassie state, i.e. a state where the grooves of the surface pattern are not wetted by water.[20] A well-known example of such a surface is the leaf of the Lotus plant,[21] on which a water droplet sits on the tops of the micropapillae that grow on the leaf, leaving most of the surface dry. In general, if the tips of the asperities that are wetted compose only a small area fraction of a patterned surface, the wetting properties are mostly determined by the trapped air layer between water and the surface. The apparent contact angle can approach 180° as shown by the Cassie-Baxter equation

Figure 1. Due to the high contact angle and low hysteresis, water droplets easily roll off superhydrophobic surfaces. However, damage to the surface often leads to an increased contact angle hysteresis and, consequently, droplets stick to the surface.

$$\cos\theta_{app} = f\cos\theta_Y - 1 + f \qquad (2)$$

where θ_Y is the intrinsic contact angle of the surface and f is the wet area fraction. Furthermore, a small area of contact between water and the surface lowers the adhesion and ensures good mobility of water drops, qualifying the surface as superhydrophobic.

The non-wettability of a surface patterned with topography can be reduced essentially in two ways: (a) loss of roughness increases the area of contact between water and the surface, or (b) the intrinsic hydrophobicity of the surface is reduced as a result of hydrophilic contamination or damage to a hydrophobic surface layer. As a consequence, the Cassie state may become unstable or contact angle hysteresis may increase due to hydrophilic defects.

2. Mechanical Durability by Hierarchical Roughness

Many recent studies[10,22–24] use roughness at two length scales to ensure that a stable Cassie state remains even after some surface features are worn away. Such morphology involves robust microscale bumps that provide protection to a more fragile nanoscale roughness that is superimposed on the larger pattern. The Cassie state is greatly stabilized by the presence of two roughness scales, and the microscale features do not need to have as large an aspect ratio as they would need if no nanostructures were present. Thus, the microroughness can be optimized with mechanical stability in mind while the nanoroughness ensures non-wettability. This concept is illustrated in **Figure 2**.

Zimmermann et al.[10] grew a layer of superhydrophobic silicone nanofilaments on textile fibers to obtain a hierarchically rough superhydrophobic fabric, shown in **Figure 3**a. Although the nanofilaments as such are very fragile and can easily be wiped away, the coated textile kept its superhydrophobic character after prolonged wear with simulated skin contact, involving a force of 5 N. The effect of wear was quantified with the water shedding angle, which is the tilt angle above which a

Dr. Robin H. A. Ras is a research group leader at the Department of Applied Physics at Aalto University (formerly Helsinki University of Technology, Finland). He obtained a PhD degree in Bioscience Engineering–Chemistry from University of Leuven (Belgium) under supervision of Prof. Robert Schoonheydt. Since 2004 he works in the lab of Prof. Olli Ikkala at Aalto University. His research interests are bio-inspired functional materials, nanoscale inorganics and superhydrophobicity.

Tuukka Verho is a graduate student under the supervision of Acad. Prof. Olli Ikkala and Dr. Robin Ras in the Department of Applied Physics of Aalto University (Helsinki, Finland). He has worked on fields ranging from first principles simulations of molecular adsorption to supramolecular self-assembly and has coauthored articles in Phys. Rev. B and Macromolecules. His present research activities involve non-wettability and biomimetic functional materials.

water drop is shed by the surface after falling from a predefined height. 1450 cycles of wear led to an increase of the shedding angle from 2° to 25°, illustrating that the abrasion nonetheless makes the surface more sticky towards water. A SEM image (Figure 3b) showed that nanofilaments were worn off from the contact surfaces but were intact elsewhere.

Another demonstration of the concept was presented by Xiu et al.,[22] who prepared two-tier roughness on silicon (Figure 3c)
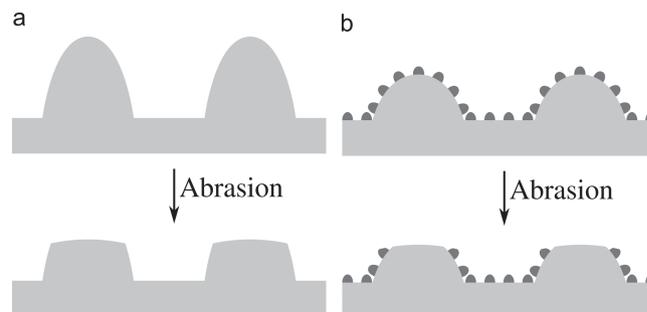

Figure 2. The effect of wear on surfaces with topography in one or two length scales. (a) Only microroughness is present. Abrasion causes the bumps to wear off, making the Cassie state no longer stable. (b) The pattern consists of shallow, mechanically stable microbumps with a nanoroughness on them. Most of the nanoroughness is unaffected by wear and the Cassie state remains stable.
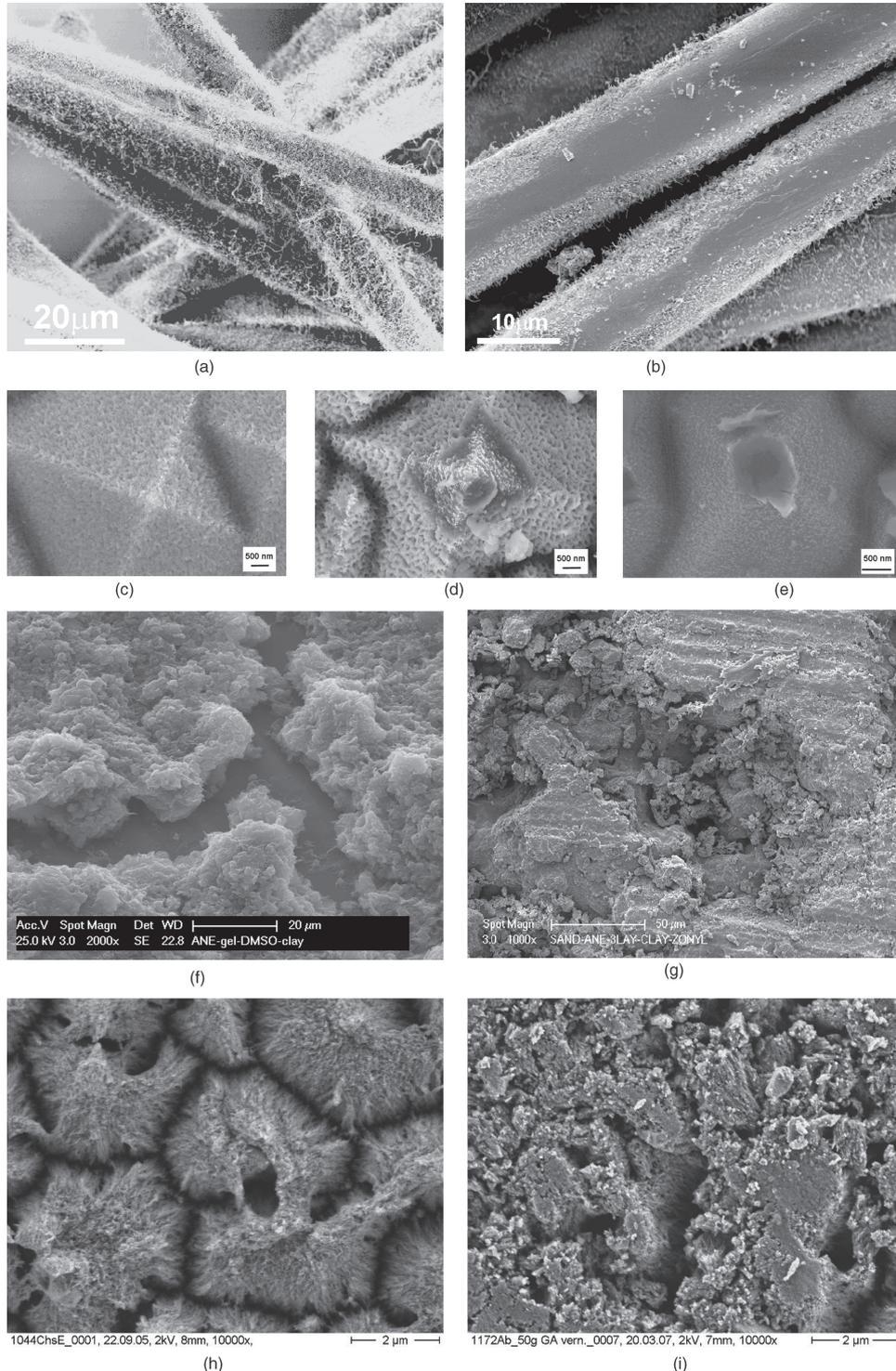
Figure 3. (a,b) PET fabric coated with nanofilaments before and after a wear test that simulates skin contact. Reproduced with permission.[10] (c) A hierarchically rough wet etched silicon surface (d) after rubbing with Technicloth wipe and (e) after sand abrasion. Reproduced with permission from IOP.[22] (f,g) An organoclay-polymer nanocomposite before and after abrading with sand paper. Reproduced with permission from APEX/JJAP.[25] (h,i) A rough alumina surface reinforced with a chitosan layer, before and after rubbing with velvet. Reproduced with permission.[26]

by first etching with KOH to create microscale pyramids and then using Au nanoparticle catalyzed HF/H_2O_2 etching to fabricate nanostructures on the pyramids, followed by a fluorination treatment to render the hydrophilic silicon surface hydrophobic. The durability of the surface features were tested by drawing the sample on a Technicloth wipe under a load of 3.5 kPa.
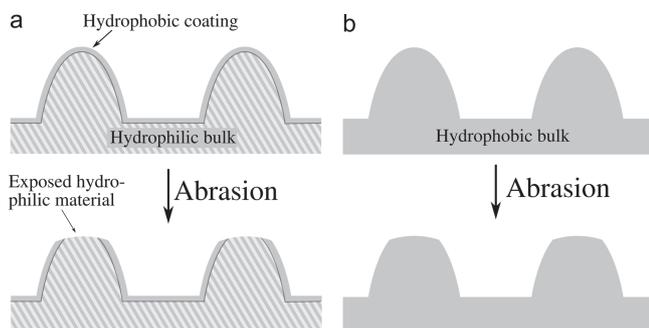
Figure 4. (a) A hydrophobic surface coating on a roughness pattern may get easily worn off, and hydrophilic bulk material will be exposed as a result. (b) If the roughness features are fabricated of hydrophobic material, wear will not introduce hydrophilic pinning sites.

Despite an increase in contact angle hysteresis the surface remained non-wettable, showing that the microscale pyramids protected the nanoscale features on the walls of the pyramids (Figure 3d).

3. Problems with Hydrophilic Bulk Materials

Most of the materials conventionally used for creating patterned surface topographies are hydrophilic. A special hydrophobic surface coating is required to make such surfaces superhydrophobic. This approach has a disadvantage that is demonstrated in the study by Xiu et al. mentioned above: when the surface was rubbed against sandpaper, a layer of material was worn off from the tops of the micropyramids, exposing the hydrophilic silicon — see Figure 3e. The receding contact angle of silicon oxide is 0°, which means that water sticks to the tops of the abraded micropyramids and non-wettability is lost even though the Cassie state is still stable. This effect is illustrated schematically in **Figure 4**a.

An obvious way to tackle the above problem is to prepare the roughness from materials that are hydrophobic to start with, eliminating the need for a hydrophobic surface layer (see Figure 4b). Bayer et al.[25] prepared spray-cast polymer-clay composite films using anaerobic acrylic adhesives to create fractal-like roughness, shown in Figure 3f. This time, polishing with sandpaper under a load of 6 kPa increased the contact angle hysteresis only from 4° to 10° even though scanning electron microscopy (Figure 3g) showed that the surface had suffered considerable damage.

Höhne et al.[26] took an interesting approach to fabricating a mechanically stable, rough surface with a hydrophobic bulk material. An aluminum surface was first oxidized anodically to yield microbumps of nanoporous alumina (Figure 3h). Chitosan was used for reinforcing the structure, deposited either electrochemically or by spin coating, and the film was rendered hydrophobic with covalently bonded hydrophobic polymer. Chitosan and polymer turned out to deposit into the nanopores of the alumina layer, effectively turning the brittle hydrophilic alumina into a mechanically stable hydrophobic composite. Abrasion testing was conducted with a rod covered with a polishing velvet. The rod was turned once with its face pressed against the surface under a pressure of 12.7 kPa. Although a visible

trace was left by the abrasion (see Figure 3i), water droplets still rolled off the surface.

4. Methods of Testing and Characterizing Wear

Objective comparison of the abrasion resistance of superhydrophobic surfaces has been hampered by the lack of a single, standardized test method. Most studies utilize custom-built in-house apparatus that involve rubbing the specimen against some kind of cloth,[22,24,26] sandpaper[22,25,27] or synthetic leather[10] under a certain load. Other procedures include ball-on-disk tests,[23] high-speed current scouring or water jet test[23,28] and rubbing with a cotton swab.[29] Likewise, no single measure has been used for characterizing the effect of wear. Different criteria used in the literature include the change in contact angle hysteresis,[22,25] water shedding angle,[10] roll-off behavior,[26,29] coefficient of friction[23] or static contact angle.[24]

5. Self-Healing Surfaces

Unlike man-made superhydrophobic surfaces, natural superhydrophobic plant leaves and insect wings can sustain their non-wettability over their whole lifetime. Their ability to withstand damage is typically based on continuous renewal of the surface as a result of biological growth processes. Mimicking this self-healing functionality[30] in artificial superhydrophobic surfaces is an interesting prospect, as suggested by Youngblood et al.[31] and Nosonovsky and Bhushan.[32]

Natural hydrophobic leaves are able to regenerate their hydrophobic epicuticular wax layer[33] and mimicking this ability to restore the surface functionality[34] can help prevent the exposure of hydrophilic bulk material on man-made non-wetting surfaces. Li et al.[27] demonstrated a superhydrophobic film with a self-healing hydrophobic surfactant coating that relies on the tendency of the film to minimize its surface energy. During the deposition of a hydrophobic silane surfactant layer, an excess of surfactant was used so that a large amount of silane was absorbed within the bulk film. When mechanical damage or chemical modification rendered the surface hydrophilic, the absorbed silane diffused, in the presence of humidity, onto the surface so as to minimize its surface energy and effectively restored the damaged hydrophobic layer. The surfactant reservoir enabled the hydrophobic layer to be restored many times. Combined with good mechanical properties of the layer-by-layer deposited hierarchically rough film, the self-hydrophobizing capability of the surface enabled a good resistance against mechanical degeneration, as was demonstrated by first scratching the film with sandpaper, consequently making water stick on it, and subsequently restoring its non-wettability by exposing it to a humid atmosphere.

For the prevention of loss of roughness, a self-repairing topography would be needed. Such a surface would be able to regenerate the surface patterns either as a result of the wear itself or with the aid of an external stimulus, such as a treatment that initiates a chemical reaction in the surface layer. We are not aware of any studies reporting such roughness-regenerating functionality as yet, however, we mention as an example of a

Materials
Views
www.MaterialsViews.com

ADVANCED
MATERIALS
www.advmat.de

RESEARCH NEWS

possible approach towards such a goal the work by Basu et al.[29] In the study, a spray-coated superhydrophobic film was created from a composite of hydrophobically modified silica particles in a fluorinated polymer matrix. The film was superhydrophobic after spray coating without further treatments. The wear resistance of the film was demonstrated with a cotton swab rubbing test. It could be speculated that such a film might exhibit some roughness-regenerating capability, since removing a layer of material might expose a new rough surface due to the silica particles embedded in the material — although this possibility was not brought up by Basu et al.

6. Particle and Organic Contamination

The susceptibility of superhydrophobic surfaces towards particle contamination is reduced by the self-cleaning effect: when the surfaces are rinsed with water, the liquid forms into droplets that collect dirt from the surface during rolling off.[21,35] Bhushan et al.[36] found that the effect depends on the tilt of the surface and on the kinetic energy of water. Also, nanostructures and hierarchical structures exhibit more efficient self-cleaning than microstructures.

Despite the self-cleaning effect, not all dirt can always be washed away with water. It has been shown that long exposure to outdoor conditions leads to gradual degradation of non-wetting surfaces.[37–41] Outdoor contamination has been thoroughly studied by Zimmermann et al.,[40] who weathered their silicone nanofilament film under rainfall over a period of one year. The loss of non-wettability was apparent as a slow increase in the roll-off angle during the first 6 months. At the end, parts of the coating were covered with organic contaminants that could not be removed by the self-cleaning effect.

Nakajima et al.[37] used the photocatalytic effect to facilitate decomposition of adhering dirt particles. Usually the presence of titanium dioxide on a surface causes a transition to a superwetting state when exposed to UV irradiation. However, Nakajima found that a small amount of TiO_2 did not cause such a transition but still enabled the photocatalytic cleaning effect. Later, Yoshida et al.[38] obtained similar results with an apatite-based catalyst. Furthermore, Sasaki et al.[39] demonstrated that reducing the electrical resistance of a superhydrophobic film discourages electrostatic attraction between the surface and contaminants and increases the lifetime of the surface.

While superhydrophobic surfaces repel water, organic liquids typically wet such surfaces completely because of their much smaller surface tension. For instance, grease from fingers will spread on superhydrophobic surfaces and is difficult to remove. However, omniphobic (also called amphiphobic, oleophobic or hygrophobic[42]) surfaces exhibit a more general repellency.[43–45] Non-wettability towards liquids with a low surface tension is achievable with re-entrant surface topologies.[42,43] Evidently, fabricating omniphobic surfaces is challenging, probably even more so if mechanically robust structures are desired.

7. Outlook

In principle, superhydrophobic surfaces possess incredibly useful properties in terms of repelling water and dirt. Yet, most commercial coatings promising to be non-wettable and easy to

clean rely solely on chemically modified low-energy surfaces and have no surface topography. The reason lies in the fact that while microscopic roughness gives rise to the Cassie state and offers the possibility of extreme non-wettability and efficient self-cleaning, it can also turn against itself. The micro- and nanostructures are easily damaged, and mechanical wear can cause water to stick on the surface. Moreover, should the self-cleaning effect fail, there is no hope of removing the dirt from between the roughnesses with mechanical rubbing.

Recently, promising results give a reason to expect that the obstacles regarding mechanical durability can be overcome. Currently, however, quantitative assessment of the mechanical durability of non-wetting surfaces is difficult due to the diversity of wear testing and characterization methods discussed above. Ideally, one standardized testing procedure would be beneficial for focused efforts to develop resilient coatings. Nevertheless, the range of possible applications for superhydrophobic surfaces may call for specialized mechanical tests. To illustrate, one could imagine superhydrophobic airplane wings that prevent ice formation,[14] superhydrophobic anti-fogging windows[13] or superhydrophobic cotton fabric that withstands laundering.[12] The plastron between a superhydrophobic surface and water could be used for microfluidic devices with slipping channel boundaries[16] or for ship hulls that have minimal drag in water — or even for underwater breathing like some aquatic insects do.[46] All these scenarios involve different challenges in terms of mechanical durability.

Still, perhaps the most appealing use for superhydrophobic surfaces is in the prevention of adhesion of dirt[8] or microbes.[47] This feature could be exploited in paints, cars or medical appliances, for example. However, superhydrophobic surfaces are not, in general, resistant against all kinds of stains, and the oily substances that reside on human skin — particularly on fingers — present a significant problem. Such liquids tend to wet superhydrophobic surfaces completely due to their low surface tension. For touchable self-cleaning surfaces one needs surfaces that repel also nonpolar liquids. On the other hand, if such an omniphobic surface with enough mechanical robustness could be fabricated, it could find a vast range of uses as a fingerprint resistant coating. The low adhesion of fingerprint residues on such a surface would enable easy removal of stains from devices such as touch displays, which are becoming ubiquitous in mobile and other appliances.[48]

Following the substantial number of papers on mechanically durable superhydrophobic surfaces that have emerged recently, we hope to see a similar rise in the research of contamination resistant non-wetting surfaces. So far, the issue of accumulation of surface contaminants in an outside-the-laboratory environment has not received the attention it deserves. Typically, it is reported that a surface has the self-cleaning property solely on the grounds that it is superhydrophobic; the actual range of particles that can be removed by rinsing with water has not been systematically determined.

8. Conclusion

Mechanical robustness is of prime importance in many applications of superhydrophobic surfaces. Recently, several studies

RESEARCH NEWS

have addressed this issue by introducing hierarchical roughness structures to reduce damage to the surface roughness features and by avoiding hydrophilic bulk materials that can cause increased sticking of water. Furthermore, it has been demonstrated that a surface can possess a self-healing capability that enables it to recover its hydrophobic layer, and it can be expected that there will be considerable interest in superhydrophobic coatings with an ability to restore its roughness or hydrophobic surface layer after damage.

Thanks to the self-cleaning effect, dirt can usually be removed from a superhydrophobic surface just by washing with water. However, when unwashable contamination eventually accumulates on the surface, non-wettability will be lost. The photocatalytic effect or improved electrical conductivity can be used to improve the self-cleaning properties. However, only a few studies have examined in detail the degradation of superhydrophobic surfaces as a result of exposure to environmental conditions. A more general non-wettability, omniphobicity, protects the surface from getting stained by organic liquids; however, a re-entrant roughness pattern is then required, which poses a challenge to fabrication and is likely to be more fragile.

If the issues regarding the lifetime of superhydrophobic surfaces in real-life uses can be solved, there are a great many potential ways to exploit the appealing properties of the Cassie state in applications. The recent progress in the development of mechanically robust superhydrophobic surfaces suggests that rough non-wetting surfaces might soon be ready for the market in terms of mechanical durability. However, the limitations of the self-cleaning effect and accumulation of impurities require more research before the widest range of applications can be realized.

Acknowledgements

[1] X. Li, D. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.* **2007**, *36*, 1350.
[2] F. Xia, L. Jiang, *Adv. Mater.* **2008**, *20*, 2842.
[3] X. Zhang, F. Shi, J. Niu, Y. Jiang, Z. Wang, *J. Mater. Chem.* **2008**, *18*, 621.
[4] J. Genzer, A. Marmur, *MRS Bull.* **2008**, *33*, 742.
[5] M. Liu, Y. Zheng, J. Zhai, L. Jiang, *Acc. Chem. Res.* **2010**, *43*, 368.
[6] D. Quéré, *Annu. Rev. Mater. Res.* **2008**, *38*, 71.
[7] M. Ma, R. M. Hill, G. C. Rutledge, *J. Adhesion Sci. Technol.* **2008**, *22*, 1799.
[8] A. Solga, Z. Cerman, B. F. Striffler, M. Spaeth, W. Barthlott, *Bioinsp. Biomim.* **2007**, *2*, S126.
[9] L. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 5998.
[10] J. Zimmermann, F. A. Reifler, G. Fortunato, L. Gerhardt, S. Seeger, *Adv. Funct. Mater.* **2008**, *18*, 3662.
[11] W. Choi, A. Tuteja, S. Chhatre, J. M. Mabry, R. E. Cohen, G. H. McKinley, *Adv. Mater.* **2009**, *21*, 2190.
[12] B. Deng, R. Cai, Y. Yu, H. Jiang, C. Wang, J. Li, L. Li, M. Yu, J. Li, L. Xie, Q. Huang, C. Fan, *Adv. Mater.* DOI: 10.1002/adma.201002614.
[13] X. Gao, X. Yan, X. Yao, L. Xu, K. Zhang, J. Zhang, B. Yang, L. Jiang, *Adv. Mater.* **2007**, *19*, 2213.
[14] L. Cao, A. Jones, V. Sikka, J. Wu, *Langmuir* **2009**, *25*, 12444.
[15] Q. Pan, M. Wang, *ACS Appl. Mater. Interfaces* **2009**, *1*, 420.
[16] J. Ou, B. Perot, J. P. Rothstein, *Phys. Fluids* **2004**, *16*, 4635.
[17] C. Furmidge, *J. Colloid Sci.* **1962**, *17*, 309.
[18] W. Zisman, *Adv. Chem. Ser.* **1964**, *43*, 1.
[19] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, *Langmuir* **1999**, *15*, 4321.
[20] A. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
[21] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1.
[22] Y. Xiu, Y. Liu, D. W. Hess, C. P. Wong, *Nanotechnology* **2010**, *21*, 155705.
[23] Y. Jung, B. Bhushan, *ACS Nano* **2009**, *3*, 4155.
[24] T. Yanagisawa, A. Nakajima, M. Sakai, Y. Kameshima, K. Okada, *Mater. Sci. Eng. B* **2009**, *161*, 36.
[25] I. S. Bayer, A. Brown, A. Steele, E. Loth, *Appl. Phys. Express* **2009**, *2*, 5003.
[26] S. Höhne, C. Blank, A. Mensch, M. Thieme, R. Frenzel, H. Worch, M. Müller, F. Simon, *Macromol. Chem. Phys.* **2009**, *210*, 1263.
[27] Y. Li, L. Li, J. Sun, *Angew. Chem. Int. Ed.* **2010**, *49*, 6129.
[28] Z. Cui, Q. Wang, Y. Xiao, C. Su, Q. Chen, *Appl. Surf. Sci.* **2008**, *254*, 2911.
[29] B. Basu, A. Paranthaman, *Appl. Surf. Sci.* **2009**, *255*, 4479.
[30] R. P. Wool, *Soft Matter* **2008**, *4*, 400.
[31] J. P. Youngblood, N. R. Sottos, C. Extrand, *MRS Bull.* **2008**, *33*, 732.
[32] M. Nosonovsky, B. Bhushan, *Appl. Surf. Sci.* **2010**, *256*, 3982.
[33] K. Koch, B. Bhushan, H.-J. Ensikat, W. Barthlott, *Phil. Trans. R. Soc. A* **2009**, *367*, 1673.
[34] D. Shchukin, H. Möhwald, *Small* **2007**, *3*, 926.
[35] R. Fürstner, W. Barthlott, C. Neinhuis, P. Walzel, *Langmuir* **2005**, *21*, 956.
[36] B. Bhushan, Y. Jung, K. Koch, *Langmuir* **2009**, *25*, 3240.
[37] A. Nakajima, K. Hashimoto, T. Watanabe, K. Takai, G. Yamauchi, A. Fujishima, *Langmuir* **2000**, *16*, 7044.
[38] N. Yoshida, M. Takeuchi, T. Okura, H. Monma, M. Wakamura, H. Ohsaki, T. Watanabe, *Thin Solid Films* **2006**, *502*, 108.
[39] M. Sasaki, N. Kieda, K. Katayama, K. Takeda, A. Nakajima, *J. Mater. Sci.* **2004**, *39*, 3717.
[40] J. Zimmermann, F. A. Reifler, U. Schrade, G. Artus, S. Seeger, *Colloids Surf., A* **2007**, *302*, 234.
[41] M. Manca, A. Cannavale, L. De Marco, A. Arico, R. Cingolani, G. Gigli, *Langmuir* **2009**, *25*, 6357.
[42] A. Marmur, *Langmuir* **2008**, *24*, 7573.
[43] A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science* **2007**, *318*, 1618.
[44] A. Ahuja, J. Taylor, V. Lifton, A. Sidorenko, T. Salamon, E. Lobaton, P. Kolodner, T. Krupenkin, *Langmuir* **2008**, *24*, 9.
[45] Y. Liu, Y. Xiu, D. Hess, C. Wong, *Langmuir* **2010**, *26*, 8908.
[46] M. R. Flynn, J. W. M. Bush, *J. Fluid Mech.* **2008**, *608*, 275.
[47] J. Genzer, K. Efimenko, *Biofouling* **2006**, *22*, 339.
[48] O. Ikkala, M. Heino, in *Nanotechnologies for Future Mobile Devices* (Eds. T. Ryhänen, M. A. Uusitalo, O. Ikkala, A. Kärkkäinen), Cambridge University Press, **2010**, pp. 21–50.