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Wettability of natural superhydrophobic surfaces

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A R T I C L E   I N F O

A B S T R A C T

Since the description of the 'Lotus Effect' by Barthlott and Neinhuis in 1997, the existence of superhydrophobic surfaces in the natural world has become common knowledge. Superhydrophobicity is associated with a number of possible evolutionary benefits that may be bestowed upon an organism, ranging from the ease of dewetting of their surfaces and therefore prevention of encumbrance by water droplets, self-cleaning and removal of particulates and potential pathogens, and even to antimicrobial activity. The superhydrophobic properties of natural surfaces have been attributed to the presence of hierarchical microscale (>1 μm) and nanoscale (typically below 200 nm) structures on the surface, and as a result, the generation of topographical hierarchy is usually considered of high importance in the fabrication of synthetic superhydrophobic surfaces. When one surveys the breadth of data available on naturally existing superhydrophobic surfaces, however, it can be observed that topographical hierarchy is not present on all naturally superhydrophobic surfaces; in fact, the only universal feature of these surfaces is the presence of a sophisticated nanoscale structure. Additionally, several natural surfaces, e.g. those present on rose petals and gecko feet, display high water contact angles and high adhesion of droplets, due to the pinning effect. These surfaces are not truly superhydrophobic, and lack significant degrees of nanoscale roughness. Here, we discuss the phenomena of superhydrophobicity and pseudo-superhydrophobicity in nature, and present an argument that while hierarchical surface roughness may aid in the stability of the superhydrophobic effect, it is nanoscale surface architecture alone that is the true determinant of superhydrophobicity.

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Contents

1. Introduction

The wetting behaviour of natural superhydrophobic surfaces has been studied for well over half a century [1–4]. Many organisms have now been identified to possess superhydrophobic structures, most notably a large number of plants and insects [5–15]. The most famous of these, and perhaps the archetype for natural superhydrophobic surfaces, is the lotus leaf [16]. Natural surfaces such as this have inspired the fabrication of countless synthetic analogues in an attempt to reproduce the extremely low wettability and other associated desirable properties of these substrata [17–21]. Given their significance as the templates on which new superhydrophobic materials are based, it is the intention of this review to discuss the mechanisms of superhydrophobicity with respect to natural surfaces, and identify the factors that make them extremely effective at repelling water.

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1.1. Evolutionary benefits associated with low wettability

From an evolutionary perspective, there are several benefits associated with the ability to repel water. First and foremost, the ability to easily shed droplets prevents an organism from becoming encumbered by water [13,22]. This is highly relevant to many insects, especially those that live in or near aquatic environments. Adhesion of water droplets increases the load an insect must bear, and therefore increases the energy that needs to be expended for locomotion. The associated consequences are obvious, ranging from the inability to evade predators to the inability for the insect to successfully forage.

The second major benefit is the 'self-cleaning' effect that is bestowed through the condition of superhydrophobicity. The low adhesion of water to a superhydrophobic surface enables the droplet to roll/slide across the surface with ease, and in the process sweep away contaminating particles through adsorption or absorption [10,23]. The archetype lotus leaf is the prime example of this effect; it has long been renowned for its ability to stay clean under a range of environmental conditions [16,24]. This means that in addition to repelling water, superhydrophobicity allows an organism to repel foreign particles, such as dirt, dust and fungal spores.

2. Contributing factors that determine hydrophobicity

The hydrophobicity of a surface can be measured as a function of the water contact angle [25–27]. It is a continuous scale that ranges from a contact angle of 0° for a surface that is able to be completely wet by water, to 180° for a surface that is completely non-wetting in nature. Therefore, the classification of surfaces as being superhydrophobic, hydrophobic, hydrophilic or superhydrophilic is somewhat arbitrary. Nevertheless, for the sake of an intuitive understanding of these definitions, it is useful to define the range of water contact angles that apply for each category. It is generally accepted that the water contact angle on a superhydrophilic surface is between 0° and 10°, a hydrophilic surface between 10° and 90°, a hydrophobic surface between 90° and 150°, and for superhydrophobic surfaces, a contact angle in excess of 150° is observed [28–32]. It has been suggested that 65° may be a more appropriate boundary to distinguish hydrophobicity from hydrophilicity [32], however 90° is the more commonly adopted contact angle for this definition. In addition, it is generally accepted that to be categorised as a superhydrophobic surface, a surface should also display low degrees of contact angle hysteresis together with a low sliding angle [33,34].

Two main wetting regimes have been accepted throughout the literature, i.e. the Wenzel and Cassie–Baxter wetting regimes [2,3]. Briefly, in the Wenzel regime, a water droplet is said to penetrate and wet the spaces between the features on a rough surface. In this case, the cosine of the observed contact angle, θ, is expressed as a function of the Wenzel roughness factor, r, and the theoretical contact angle of a water droplet on an ideal smooth surface of the same component material, θ_{smooth}:

$$\cos\theta = r\cos\theta_{smooth}.$$

In the Cassie–Baxter regime, the inability of water to fully penetrate between the surface features leads to the entrapment of air pockets, which in turn increases the observed water contact angle. In this case, the cosine of the observed angle is described as a function of the area fraction of the solid/liquid interface on the contact line, f, and θ_{smooth}:

$$\cos\theta = f(\cos\theta_{smooth} + 1) - 1.$$

The Wenzel and Cassie–Baxter wetting regimes have both been extensively utilised and reported throughout the literature, and it is generally assumed that any water droplet on a rough surface is in either the Wenzel or Cassie–Baxter state, or an intermediate between the two, sometimes referred to as a 'Cassie-impregnating' state [35,36].

The chemical composition of a surface is also well known to be the second contributing factor in determining the wettability of a surface [2,3,37,38]. Its effects are substantial when the wettability of a smooth surface is being considered, however with increasing surface roughness, the physical structure plays an increasingly important role in the determination of the observed contact angle [1,2]. When considering surface wetting in the Cassie–Baxter state, it is at least theoretically possible to achieve a water contact angle of 150° on a material that, if smooth, would otherwise be wet completely, provided that the solid/liquid interface fraction is limited to approximately 0.07 (Fig. 1). While this is likely to be impossible to achieve in practice, it serves to demonstrate the important contribution of surface structure to the superhydrophobicity of a surface. It is notable that in the case of the feet of water striders in contact with water, the solid/liquid interface fraction has been reported to be as low as 0.03 [39]. For these reasons, the surface structure and topography of natural superhydrophobic surfaces will be the primary focus of this review.

3. Superhydrophobic structures found in nature

3.1. Plants

Plants are by far the best-characterized of all the organisms that have been identified to possess superhydrophobic surfaces. The works of Neinhuis, Barthlott, Bhushan and Koch have provided a great insight, together with a systematic analysis, into the various surface structures amongst plants from diverse habitats [5,7,16,24,40–44]. Generally speaking, the structure of the outer surface of plants is determined by a combination of two factors: the morphology of the epidermal cells in question, and the layer of cuticular waxes and lipids usually present on the external extremity of the surface [5,30]. Both the epidermal cells and cuticular waxes can exhibit a variety of morphologies, the combination of which can result in a diverse range of surface architectures.

In 1998, Barthlott et al. developed a classification system for the description of plant cuticular wax structures [5]. According to this system, cuticle wax morphologies can be grouped into two main categories, each containing several sub-groupings. The first category is the layers and films, which generally consist of relatively flat, homogeneous coatings on the surfaces of plants (Fig. 2a–d). These structures can be further sub-classified as films, smooth layers, fissured layers and crusts, primarily according to the thickness of the wax layer and its tendency to form cracks and fissures on drying. The second category of wax structures, however, is far more relevant to superhydrophobic phenomena, as all known superhydrophobic plant structures belong to this group. They are the wax crystals, and many different crystal morphologies have been described in the literature [41–43,45–47]. The wax crystals can be further divided into plates/platelets, and rodlets/tubules. Platelets are flat and thin structures that are attached to the underlying substrate via one edge (Fig. 2e). They may be rounded with entire margins that can be either irregular or membranous in nature. Plates, as opposed to platelets, are often polygonal and usually have distinct edges. Rodlets, on the other hand are relatively cylindrical or slightly conical in shape (Fig. 2g). They can have a variety of cross-sections, e.g. circular or polygonal in shape, and sometimes possess transverse ridges or form coils. Tubules are similar to rodlets in terms of their size and aspect ratios, however as the name suggests, they resemble hollow cylinders (Fig. 2f). Threads are another wax crystal structure similar to rodlets, differing primarily in that they are much longer, with higher aspect ratios (Fig. 2h).

The vast majority of plants with superhydrophobic surfaces exhibit hierarchical surface features, consisting of microscale roughness (i.e. features greater than 1 μm in diameter), as a result of epidermal cell morphology, supplemented with nanoscale roughness (features less than 1 μm, typically 200 nm or less) resulting from the presence of wax crystals. The best-known example of a superhydrophobic plant surface, the lotus leaf, possesses microscale (~10 μm) papillae covered
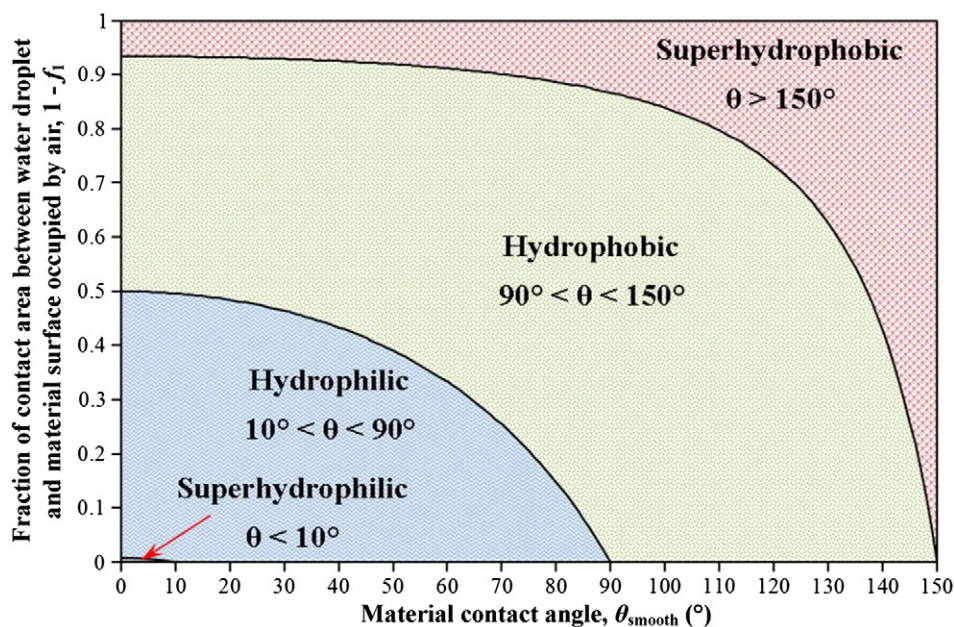
Fig. 1. The relationship between material wettability (θ_{smooth}) and the proportion of air trapped within a rough surface. According to the Cassie–Baxter model of wettability, a water droplet in contact with a rough surface will exhibit a water contact angle that is a composite of the water contact angle of the material itself and of the air/water interfacial contact angle (i.e. 180°) due to the presence of air bubbles trapped within the features of the surface.

with nanoscale wax tubules (<200 nm) [16,24,50]. Many other plants possess hierarchical structures, and a number of examples of superhydrophobic plants containing all of the major wax crystal structures are known [5,11,43,48,49]. Some plants are able to achieve superhydrophobicity with a relatively flat and smooth microstructure; the flat microstructure is compensated by the presence of dense wax crystal structures on the surface which render them superhydrophobic; however these plants typically do not retain their superhydrophobicity over their entire lifetime [5,51].

3.2. Insects

Insects are perhaps the second highest studied group of organisms that possess superhydrophobic structures. While comparably fewer systematic studies have been conducted on insect surface structures compared to that of plants, many papers have reported the superhydrophobic nature of various insect wings [13,52–58], and some works have attempted to classify insect cuticles present on the wings according to their structure. Notably, Byun et al. characterized the surface structures of the wings of 24 different species of insects from across 10 orders, including the measurement of water contact angles [8]. They classified the wings of all tested species into one of four general cuticular structures: layered cuticles, fractal structures, denticles and setae.

Layered cuticles refer primarily to butterflies and related insects belonging to the order *Lepidoptera*. The wings of these insects typically exhibit very high water contact angles (greater than or equal to 150°), and in addition display anisotropism both in terms of their wettability and structure [9,15,59]. The wings are covered in many overlapping micro-sized (typically 10 μm–100 μm) scales oriented in the one direction, with the structure of each scale consisting of parallel ridges running along the long axis of the scale, connected by horizontal links and covered with multiple nano-sized (<1 μm) protuberances (Fig. 3a). In addition to exhibiting superhydrophobicity, the directionality of these structures also produces anisotropic wetting characteristics in that water droplets preferentially roll off of the wing in one direction [15].

Fractal structures appear more irregular and random in comparison to other cuticular structures [8,13,58]. They can be regarded as fine, irregular protrusion that appear randomly oriented and do not generally display any directionality (Fig. 3b). The individual features of fractal structured surfaces are usually quite small, i.e. sub-micron/nanoscale, which makes them particularly well-suited to maintaining the Cassie–Baxter state. As a result, much like layered cuticles, fractal structures also typically result in the superhydrophobicity of the surface [8,13,58]. Examples of superhydrophobic insects with fractal structures on their wings include the orders *Odonata* (e.g. dragonflies), *Neuroptera* (Lacewings) and *Epehemeroptera* (Mayflies).

The term 'denticle' literally describes any 'tooth-like' projections [8]. In relation to insect cuticles, denticles can be found in a variety of different morphologies, ranging from convex hemispheres to conical nanopillars (Fig. 3c). Given their variety of morphologies, denticle-structured surfaces can also exhibit a wide range of surface wettabilities, for example the surface of the wings of *Chrysomela populi* leaf beetles has been reported to possess denticle structures and exhibit water contact angles of 30° [8], while the nanopillar-type denticles on the wings of *Psaltoda claripennis* cicadae result in water contact angles of approximately 159° [57]. Superhydrophobic insects with denticle structures include members of the order *Orthoptera* (e.g. grasshoppers) and *Hemiptera* (esp. cicadae).

Setae are hair-like structures, somewhat analogous to the thread structures found in plants. They are long, narrow columns, usually tapered at the tip (Fig. 3d). Setae are generally microscale in size (e.g. 20 μm–50 μm in length), and most often are not particularly hydrophobic, let alone superhydrophobic [8]. One known exception, however, is found on the wings of a species of horsefly, *Tabanus chrysurus*, of the order *Diptera*, which were reported to exhibit water contact angles of 156° [8]. The setae on the surface of the wings of *T. chrysurus* are approximately 20 μm in length, and possess nanoscale ridges and grooves, approximately 800 nm in periodicity. These 'nanogrooves' appear to be crucial to the formation of superhydrophobic setae. By comparison, other insects with setae of similar length but without the nanogrooves being present, can typically only achieve water contact angles no more than 100° [8]. The observation that nanoscale groove structures
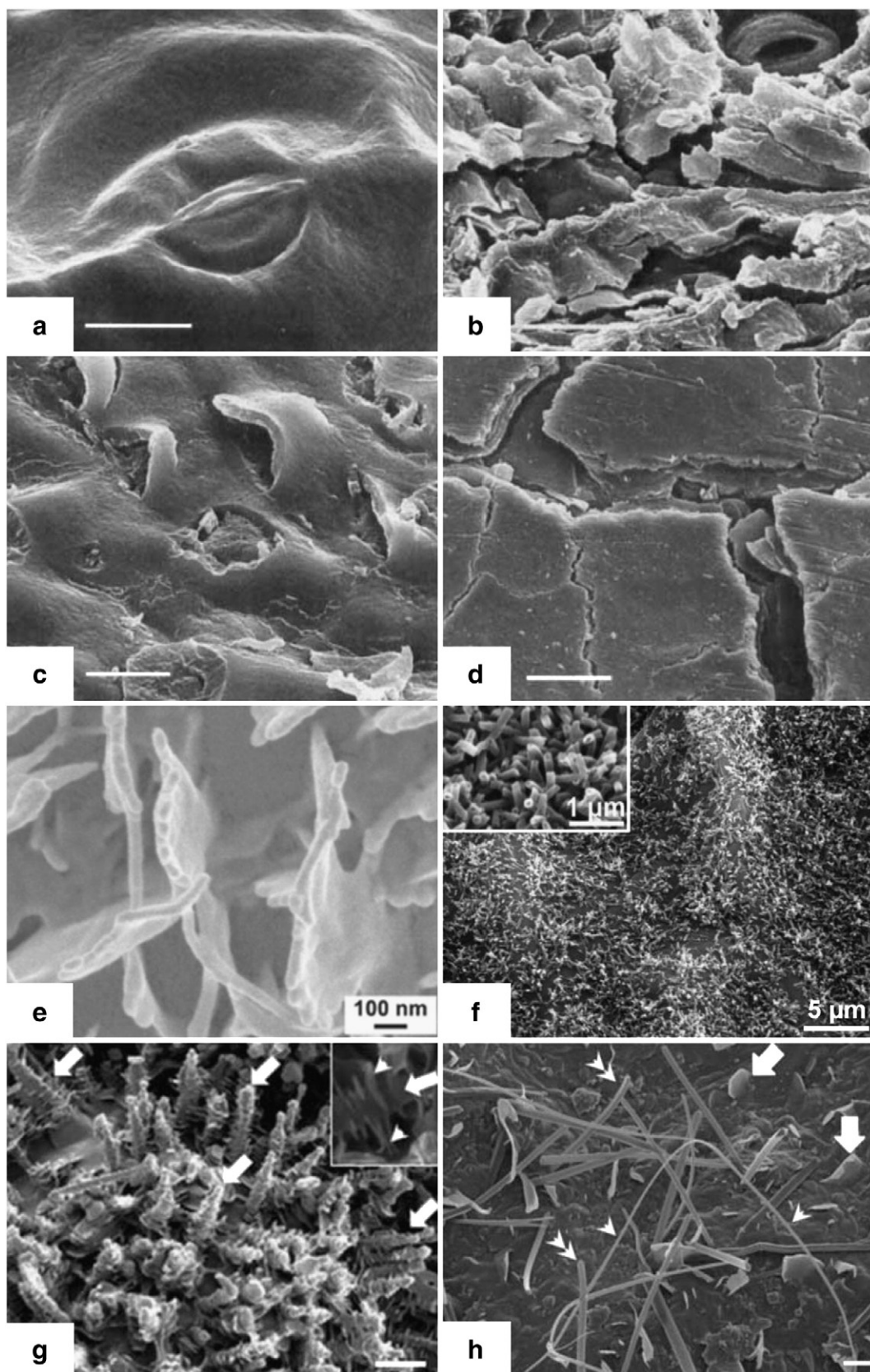
Fig. 2. Major nanoscale morphology of plant cuticular waxes. Panels a–d represent the film (scale bar = 10 μm), crust (scale bar = 20 μm), smooth layer (scale bar = 10 μm) and fissured layer (scale bar = 20 μm) morphologies, respectively. Panels e–h depict the major wax crystal morphologies, in the form of platelets, tubules, rodlets (transversely ridged rodlets show, scale bar = 2 μm) and threads (scale bar = 1 μm). Adapted with permissions from [5,11,43,48,49].
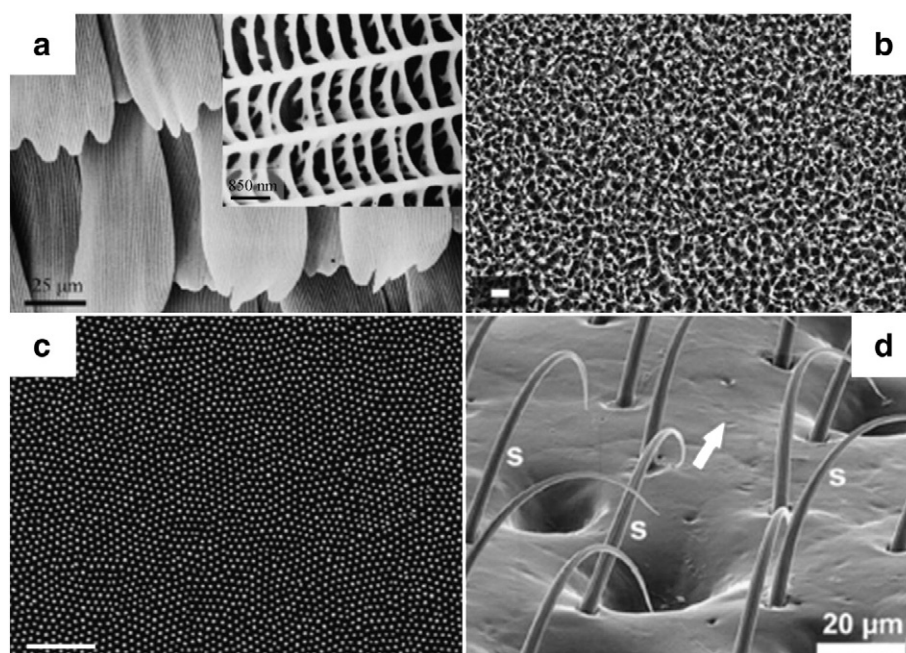
Fig. 3. Common surface nanomorphologies amongst superhydrophobic insect surfaces. The multilayered cuticles of butterfly wings consists of numerous micron-sized scales (a), oriented in the same direction, each of which is formed by cross-linked nanoscale ribs (inset). Dragonfly wings are covered by a seemingly disordered fractal structure (b, scale bar = 400 nm), which are highly effective at maintaining superhydrophobicity. In contrast, the array of highly-ordered nanopillars on the surface of cicada wings is an example of a superhydrophobic insect surface with denticle structures (c, scale bar = 2 μm). The fourth common structure amongst insect surfaces is hair-like setae, such as that of the surface of beetle elytra (d), however these structures are not usually superhydrophobic. Adapted with permissions from [13,15,54,57].

can induce superhydrophobicity on a structure that would otherwise be substantially more wettable is another indication of the importance of nanostructure in superhydrophobicity.

3.3. Pseudo-superhydrophobic organisms

There are a few organisms that are generally accepted as superhydrophobic that were not discussed in Sections 3.1 and 3.2. Rose petals and gecko feet are famous for possessing interesting properties that are not commonly found amongst the superhydrophobic materials (Fig. 4). The hierarchical surface structure of rose petals causes water droplets to strongly adhere, despite large observed contact angles [7,35,60]; and the microscale setae (~100 μm) on the soles of gecko feet are responsible for the reptile's remarkable ability to climb most types of surfaces [61–64]. There is some debate with regard to the relevant surface forces involved in the adhesion of gecko feet to surfaces, and many quality papers are available in the literature on this research [65–68], however this topic is outside the scope of this review. However, these surfaces should be only considered to be pseudo-superhydrophobic, as each of them fails to meet one of the prerequisites for superhydrophobicity; both surfaces display high droplet adhesion and hysteresis, despite having static contact angles in excess of 150° [28,30].

## 4. Metastability of superhydrophobic surfaces

The adhesion of water droplets to gecko feet and rose petals is due to significant pinning of the water droplet between the surface features, which increases the solid/liquid contact area [35,60,64,69]. A droplet in the Cassie-impregnating or Wenzel state penetrates the spaces between the surface features, and thus experiences higher adhesive force to the sample. In the case of both the gecko foot and rose petal, this pinning effect comes about as a result of the scale of the morphological features of their surfaces. Like lotus leaves, rose petals are covered with microscale papillae, however they are slightly broader (approximately 15 μm) and spaced further apart in the latter case [35,60]. In addition, the nanoscale cuticular folds (irregular periodicity, <1 μm) on the

rose petal are confined mainly to the upper regions of the papillae. As a result, water is more readily able to penetrate between the microscale structures on the surface of the petal. Similarly, the hierarchical structures on the soles of gecko feet are relatively large compared to the structures found on superhydrophobic plants and insects, and as a result, any water coming into contact with them strongly adheres to the surface [64,69].

In work reported by Zhang et al., the role of microstructure and nanostructure of surfaces in determining the static contact angle and degree of pinning of water droplets by superhydrophobic surfaces was mathematically determined [70]. In this work, microscale structures were considered in the range of 2 μm–24 μm, and nanoscale structures were regarded to be less than 10 nm. They found that the prime determining factor of the static contact angle of a surface was the dimensions of the nanoscale structures present on the surface, and that the microscale structure did not play a significant role. When the space between the nanoscale features was increased, the calculated contact angles rose slightly, before dropping sharply. Contact angles also initially rose sharply with increasing nanofeature height, and continued to approach a maximum value, however this occurred more slowly as the height of the nanofeature continued to rise. By contrast, varying the dimensions of the microscale structure had almost no effect on the static contact angle, however it was found to be the main contributor to the degree of contact angle hysteresis.

The method used by Zhang et al., in an attempt to resolve the roles played by both the nanoscale and microscale features in the wetting process, is open to interpretation, however their results agree well with the wetting behaviour that is observed in nature. The common feature amongst superhydrophobic surfaces is the presence of sophisticated nanoscale structures. It is often postulated that hierarchical roughness is necessary to achieve superhydrophobicity, however examples exist that defy this supposition. The leaves of *Brassica oleracea* do not possess substantial microscale roughness, but are covered in dense nanoscale wax crystals [5,51]. Similarly, the wings of many insects, such as cicadae and dragonflies, do not possess substantial microscale roughness but do exhibit very high water contact angles [13,57,58,71,72]. The importance of

Rose petal micro/nanostructure
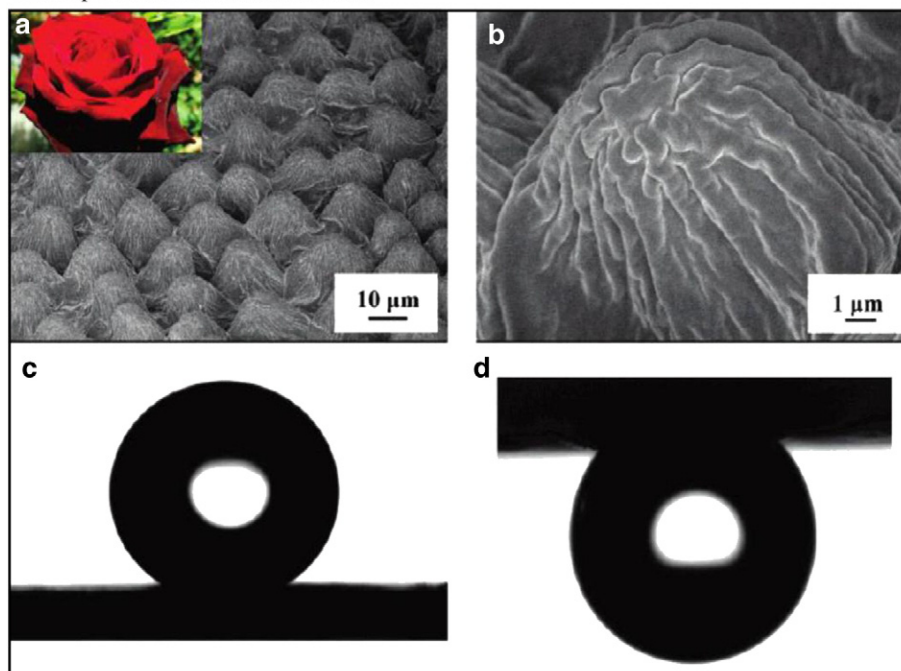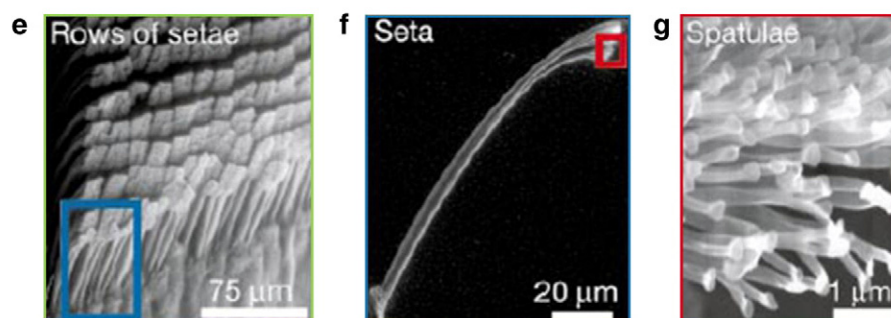

Gecko foot micro/nanostructure

Fig. 4. Pseudo-superhydrophobic natural surfaces. Rose petals possess microscale papilla structures, somewhat similar to lotus leaves, however their nanoscale structure is very different; instead of the nanotubule wax crystals found on lotus leaves, rose petal papillae are covered with nanoscale cuticular folds (a, b). As a result, water droplets on rose petal surfaces display high water contact angles in addition to high adhesion (c, d). Gecko feet are covered with a hierarchical surface in the form of arrays of setae, each of which is tipped with smaller spatulae (e–f). Gecko feet also display high adhesion to water, and thus can be considered to be pseudo-superhydrophobic. Adapted with permissions from [35,69].

nanoscale structures in determining superhydrophobicity is also evident when considering the wings of *T. chrysurus*; setae structures generally do not impart superhydrophobicity to a surface, however when the setae possess nanoscale grooves (such as in the case of *T. chrysurus*), the resulting surface becomes superhydrophobic [8]. In addition, when nanoscale structure is missing from portions of a surface, as is found on rose petals, those areas become much more wettable, which can lead to high contact angle hysteresis and greater levels of adhesion [35,60].

5. Summary and conclusions

Despite the fact that many natural superhydrophobic surfaces contain hierarchical surface roughness on the micro- and nanoscale, it is the major conclusion of this work that the presence of this topographical hierarchical roughness alone is not strictly necessary to achieve water contact angles in excess of 150°. Some plants, and many insects, possess sufficiently rough nanotopographies without substantial amounts of microscale roughness, but are able to maintain their superhydrophobicity. In some cases, such as with rose petals and gecko feet, the microscale structure is the causal factor that prevents the surface from being able to be classified as superhydrophobic, due to the establishment of strong pinning effects. It is the scale of the

surface topography that is the main contributing factor in determining wettability; in order to be regarded as superhydrophobic, a surface must be rough on a sufficiently small, i.e. nano, scale. As is so often the case with physical phenomena such as wetting, size is a key consideration.

References

[1] Cassie ABD, Baxter S. Nature 1945;155:21.
[2] Cassie ABD, Baxter S. Trans Faraday Soc 1944;40:546.
[3] Wenzel RN. J Phys Colloid Chem 1949;53:1466.
[4] Fogg GE. Nature 1944;154:515.
[5] Barthlott W, Neinhuis C, Cutler D, Ditsch F, Meusel I, Theisen I, et al. Bot J Linn Soc 1998;126:237.
[6] Barthlott W, Schimmel T, Wiersch S, Koch K, Brede M, Barczewski M, et al. Adv Mater 2010;22:2325.
[7] Bhushan B, Her EK. Langmuir 2010;26:8207.
[8] Byun D, Hong J, Saputra, Ko JH, Lee YJ, Park HC, et al. J Bionic Eng 2009;6:63.
[9] Ding Y, Xu S, Zhang Y, Wang AC, Wang MH, Xiu Y, et al. Nanotechnology 2008;19 [Art. No. 355708].

[10] Hüger E, Rothe H, Frant M, Grohmann S, Hildebrand G, Liefeith K. Appl Phys Lett 2009;95 [Art. no. 033702].
[11] Kim KW. J Electron Microsc 2012;61:433.
[12] Mele E, Girardo S, Pisignano D. Langmuir 2012;28:5312.
[13] Nguyen SH, Webb HK, Hasan J, Tobin MJ, Crawford RJ, Ivanova EP. Colloids Surf B 2013;106:126.
[14] Su Y, Ji B, Huang Y, Hwang K-C. Langmuir 2010;26:18926.
[15] Sun G, Fang Y, Cong Q, Ren L-Q. J Bionic Eng 2009;6:71.
[16] Barthlott W, Neinhuis C. Planta 1997;202:1.
[17] Neto AI, Meredith HJ, Jenkins CL, Wilker JJ, Mano JF. RSC Adv 2013;3:9352.
[18] Pechook S, Pokroy B. Soft Matter 2013;9:5710.
[19] Yang H, Dou X, Fang Y, Jiang P. J Colloid Interface Sci 2013;405:51.
[20] McCarthy M, Gerasopoulos K, Enright R, Culver JN, Ghodssi R, Wang EN. Appl Phys Lett 2012;100 [Art. no. 263701].
[21] Yan YY, Gao N, Barthlott W. Adv Colloid Interface Sci 2011;169:80.
[22] Watson GS, Cribb BW, Watson JA. ACS Nano 2010;4:129.
[23] Fürstner R, Barthlott W, Neinhuis C, Walzel P. Langmuir 2005;21:956.
[24] Bhushan B, Jung YC, Niemietz A, Koch K. Langmuir 2009;25:1659.
[25] Johnson RE, Dettre RH. Surf Colloid Sci 1969;2:85.
[26] Good RJ. Surf Colloid Sci 1979;11:1.
[27] Crawford R, Koopal LK, Ralston J. Colloids Surf 1987;27:57.
[28] Adam NK. Nature 1957;180:809.
[29] Koch K, Barthlott W. Philos Transact A Math Phys Eng Sci 2009;367:1487.
[30] Webb HK, Hasan J, Truong VK, Crawford RJ, Ivanova EP. Curr Med Chem 2011;18:3367.
[31] Ashraf M, Campagne C, Perwuelz A, Champagne P, Leriche A, Courtois C. J Colloid Interface Sci 2013;394:545.
[32] Cheng M, Liu Q, Ju G, Zhang Y, Jiang L, Shi F. Adv Mater 2014;26:306 [Early online publication].
[33] Quéré D. Rep Prog Phys 2005;68:2495.
[34] Shirtcliffe NJ, McHale G, Atherton S, Newton MI. Adv Colloid Interface Sci 2010;161:134.
[35] Feng L, Zhang Y, Xi J, Zhu Y, Wang N, Xia F, et al. Langmuir 2008;24:4114.
[36] Cho KL, Wu AH-F, Liaw II, Cookson D, Lamb RN. J Phys Chem C Nanomater Interfaces 2012;116:26810.
[37] Blomquist GJ. Structure and analysis of insect hydrocarbons. In: Blomquist GJ, Bagnères A-G, editors. Insect hydrocarbons: Biology, biochemistry, and chemical ecology. Cambridge: Cambridge University Press; 2010. p. 19.
[38] Coelho D, Marques G, Gutiérrez A, Silvestre AJD, del Río JC. Ind Crop Prod 2007;26:229.
[39] Gao X, Jiang L. Nature 2004;432:36.
[40] Bixler GD, Bhushan B. J Colloid Interface Sci 2013;393:384.
[41] Koch K, Bhushan B, Barthlott W. Soft Matter 2008;4:1943.
[42] Koch K, Bhushan B, Barthlott W. Prog Mater Sci 2009;54:137.
[43] Koch K, Dommisse A, Barthlott W. Cryst Growth Des 2006;6:2571.
[44] Neinhuis C, Barthlott W. Ann Bot 1997;79:667.
[45] Buschhaus C, Jetter R. J Exp Bot 2011;62:841.
[46] Ensikat HJ, Boese M, Mader W, Barthlott W, Koch K. Chem Phys Lipids 2006;144:45.
[47] Jetter R, Riederer M. Planta 1994;195:257.
[48] Kim KW, Koo YK, Yoon CJ. J Electron Microsc 2012;61:37.
[49] Yang S, Ju J, Qiu Y, He Y, Wang X, Dou S, et al. Small 2014;10:294 [Early online publication].
[50] Truong VK, Webb HK, Fadeeva E, Chichkov BN, Wu AHF, Lamb RN, et al. Biofouling 2012;28:539.
[51] Tan S, Xie Q, Lu X, Zhao N, Zhang X, Xu J. J Colloid Interface Sci 2008;322:1.
[52] Kreuz P, Arnold W, Kesel AB. Ann Biomed Eng 2001;29:1054.
[53] Perez Goodwyn P, Maezono Y, Hosoda N, Fujisaki K. Naturwissenschaften 2009;96:781.
[54] Sun J, Bhushan B. RSC Adv 2012;2:12606.
[55] Sun M, Liang A, Watson GS, Watson JA, Zheng Y, Ju J, et al. PLoS ONE 2012;7 [Art. no. e35056].
[56] Watson GS, Cribb BW, Watson JA. PLoS ONE 2011;6 [Art. No. e24368].
[57] Ivanova EP, Hasan J, Webb HK, Truong VK, Watson GS, Watson JA, et al. Small 2012;8:2489.
[58] Ivanova EP, Nguyen SH, Webb HK, Hasan J, Truong VK, Lamb RN, et al. PLoS ONE 2013;8 [Art. no. e67893].
[59] Fang Y, Sun G, Wang T, Cong Q, Ren L. Chin Sci Bull 2007;52:711.
[60] Teisala H, Tuominen M, Kuusipalo J. J Nanomater 2011 [Art. no. 818707].
[61] Geim AK, Dubonos SV, Grigorieva IV, Novoselov KS, Zhukov AA, Shapoval SY. Nat Mater 2003;2:461.
[62] Lee H, Lee BP, Messersmith PB. Nature 2007;448:338.
[63] Mahdavi A, Ferreira L, Sundback C, Nichol JW, Chan EP, Carter DJD, et al. Proc Natl Acad Sci U S A 2008;105:2307.
[64] Stark AY, Sullivan TW, Niewiarowski PH. J Exp Biol 2012;215:3080.
[65] Puthoff JB, Prowse MS, Wilkinson M, Autumn K. J Exp Biol 2010;213:3699.
[66] Das S, Chary S, Yu J, Tamelier J, Turner KL, Israelachvili JN. Langmuir 2013;29:15006.
[67] Liu S, Tang M, Soh A-K, Hong L. J Nano Res 2013;25:101.
[68] Stark AY, Badge I, Wucinich NA, Sullivan TW, Niewiarowski PH, Dhinojwala A. Proc Natl Acad Sci U S A 2013;110:6340.
[69] Autumn K, Liang YA, Hsieh ST, Zesch W, Chan WP, Kenny TW, et al. Nature 2000;405:681.
[70] Zhang B, Wang J, Zhang X. Langmuir 2013;29:6652.
[71] Hasan J, Webb HK, Truong VK, Pogodin S, Baulin VA, Watson GS, et al. Appl Microbiol Biotechnol 2012;97:9257.
[72] Pogodin S, Hasan J, Baulin VA, Webb HK, Truong VK, Phong Nguyen TH, et al. Biophys J 2013;104:835.