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Effects of the natural microstructures on the wettability of leaf surfaces

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Abstract

The effects of natural microstructures on the wettability are investigated based on the systematic analysis on the contact angles and morphology of the leaf surfaces of four kinds of plants, *Photinia serrulata*, Ginkgo, Aloe vera and *Hypericum monogynum*. *P. serrulata* possesses the most wettable leaf surface due to the small corrugation and raised boundary of the microstructures, while *H. monogynum* leaf shows the largest contact angle as it exhibits corrugated microstructures with smaller pitch value and larger height compared with that of Aloe vera. The long-shaped and well aligned microstructures, which are beneficial for the diffusion of water, make the Ginkgo leaf surface to be hydrophilic. The study elaborates the effects of microstructures on the surface wettability, which shed light on the design of surfaces for different wettable needs.

Keywords: Wettability; Microstructures; Leaf surface; Contact angle; Morphology

1. Introduction

Nature shows diverse vagarious functions through millions of years of evolution, intriguing much research interest in the recent few decades [1–4]. One of the most concerned functional systems refers to the superhydrophobic surface, like the leaf and petal surfaces [5,6]. Water-repellent surfaces also exit among animals, for instance, water strider [1,7], shark skin [8], butterfly wings [9] and so on. Ascribed to the fancy property and wide variety of bionic applications (such as water-proofing [10], self-cleaning [11], drag-reduction [8], anti-biofouling [12]), scientists have shown great interest in understanding the mechanism of wettability, especially the superhydrophobicity and superhydrophilicity mechanisms and imitating such surfaces [13–15].

The chemical compositions of the wax and structures on the surface are reported to be the main influencing factors on the wettability [4]. The compositions of the wax reduce the surface energy and then increase the contact angle, but the maximum contact angle can only reach 120° even on surface with extreme low energy [16]. So researchers believe that the impact of the composition of wax on the wettability is smaller, compared to the surface structures [17]. The surfaces with superhydrophobicity in nature are mostly rough and multiscale. The most notable one is the lotus leaf surface, which is superhydrophobic and self-cleaning (known as "lotus effect") [18], and exhibits microstructures covered by nanostructures on the surface. The structural effect on the surface wettability is so complicated due to the diversity of Nature that it is not fully understood yet, though continuous attention has been paid for a long period. Thus in this paper, we investigate the effects of microstructures on wettability by employing four kinds of leaf surfaces as objects. The contact angles of the surfaces are compared and the studies on the surface structures are further conducted based on the persuasive surface data. We hope the results increase our understanding of the structural effects on the surface wettability and provide useful data for the design of surfaces with different wettability.

2. Experimental methods

In this study, leaves of four kinds of plants, *Photinia serrulata*, Ginkgo, Aloe vera and *Hypericum monogynum*, which show

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different wettability are chosen for comparison. The surface morphology of the samples is analyzed using 3D laser scanning microscope (Keyence VK-X200). The wettability of the samples is characterized by the static contact angle (CA) for deionized water, which here is measured using SL-200 contact angle meter. For the convenience of contact angle measurements, the samples are finely flatted on glass slide. The deionized water droplets are strictly controlled at 5 μl. The shape of the droplet is imaged by a CCD camera and then the contact angle is calculated by the included software.

3. Results and discussion

Fig. 1 shows the contact angle values of the leaf surfaces of the four kinds of plants, *P. serrulata*, Ginkgo, Aloe vera and

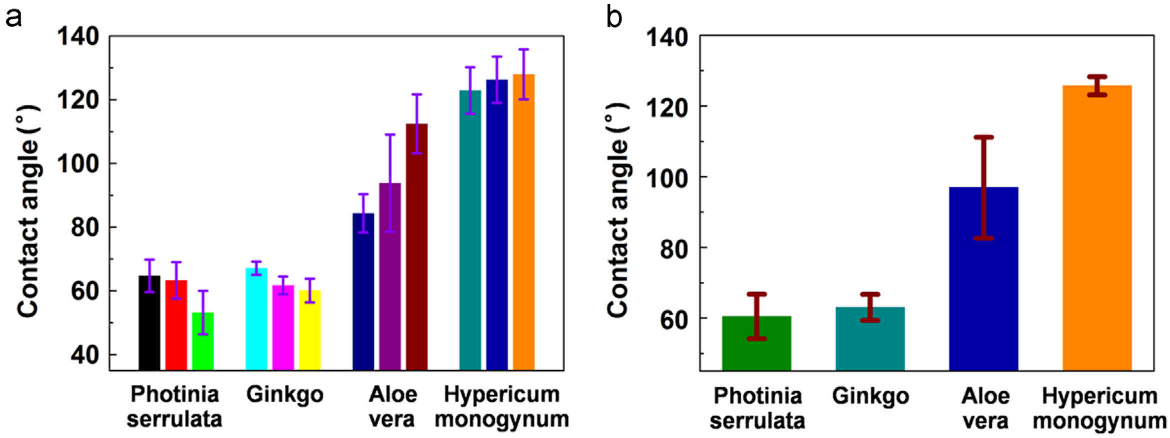

Fig. 1. (a) The contact angles of the leaf surfaces of *Photinia serrulata*, Ginkgo, Aloe vera and *Hypericum monogynum*. From the left to the right side, the three columns of each kind of plant corresponds to the contact angles measured at the regions near the root, middle and apex parts of the leaves (the left, right and root parts for Ginkgo), respectively. (b) The average contact angles obtained based on the three contact angle values in (a).

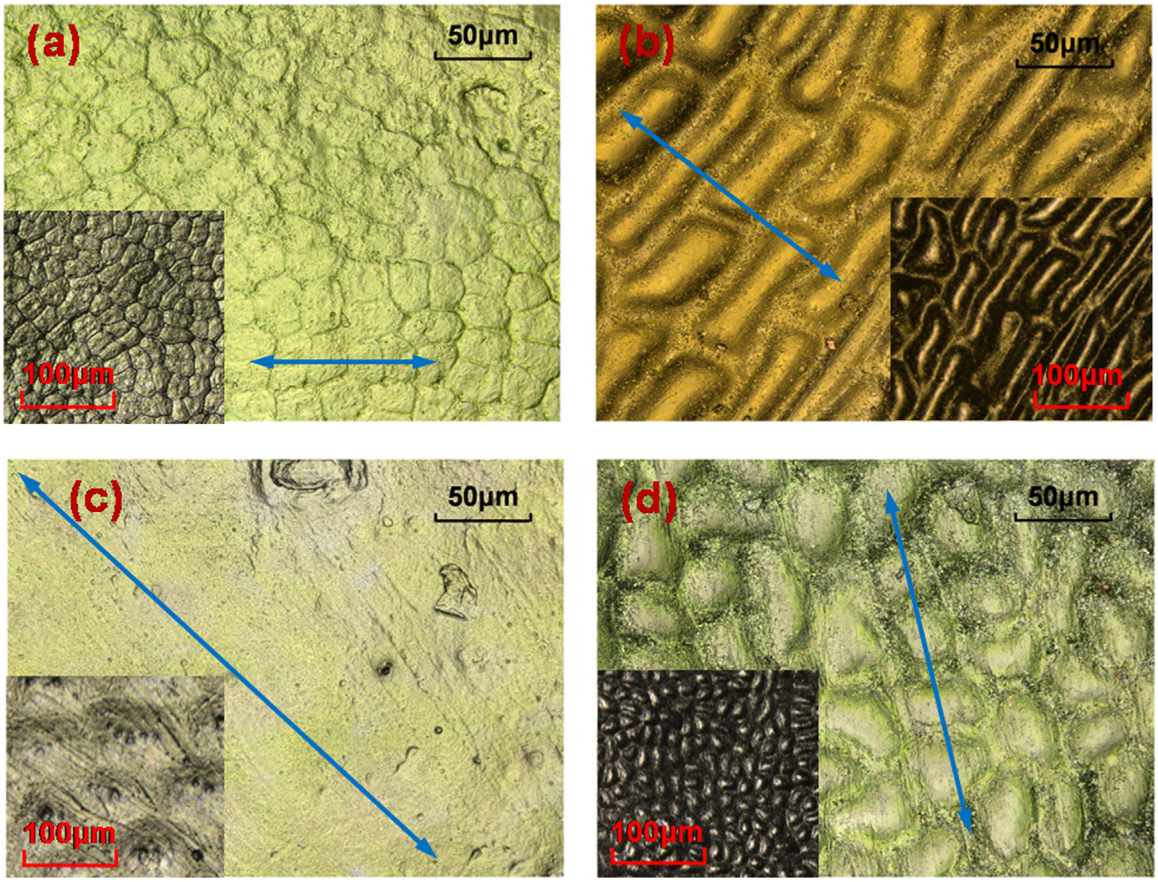

Fig. 2. The surface morphology with the magnification of one thousand times of the four kinds of plant leaves: (a) *Photinia serrulata*, (b) Ginkgo, (c) Aloe vera and (d) *Hypericum monogynum*. The insets show the morphology magnified four hundred times. The blue lines indicate the locations of the cross sections shown in Fig. 3.

H. monogynum. As shown in Fig. 1(a), for *P. serrulata*, the contact angle measured nearly the root of the leaf is the largest, and the apex part of the leaf exhibits the smallest contact angle. The Aloe vera and *H. monogynum* have the opposite situation. The root and apex part of the leaf show the smallest and largest contact angles respectively. Though the contact angles differ due to the difference of measurements location, the contact angles of each kind of plant vary overall in a certain small range. The average contact angle of each kind of plant is shown in Fig. 1(b). The *P. serrulata* leaf surface exhibits the smallest contact angle, 60.43°, while that of *H. monogynum* shows the largest contact angle, 125.70°. The contact angles of the Ginkgo and Aloe vera leaf surfaces are 63.01° and 96.89°. Generally, surfaces with contact angle smaller than 90° is hydrophilic, and that with contact angle larger than 90 is hydrophobic. So the leaf surfaces of *P. serrulata* and Ginkgo are hydrophilic, while those of Aloe vera and *H. monogynum* show different hydrophobicity. Then the question is: what is the reason for the distinct difference of wettability of the four kinds of plant leaf surfaces?

Fig. 2 shows the surface morphology of the four kinds of plants. The insets indicate the morphology magnified four hundred times. It can be seen clearly that the surfaces consist of microstructures, while the shapes of the microstructures are quite different from one another. The larger images, with the magnification of one thousand times, of the microstructures are shown in Fig. 2(a)–(d). Though shapes of the microstructures on one kind of leaf surface are a little different from one another, they share much common features and can be regarded as the same kind of microstructure, given the randomness during the growth of plant leaf. So here we obtain four kinds of microstructures, which serve as the key characteristic of their own leaf surfaces. The key feature, namely the microstructures, may be of crucial importance to the wettability of the four kinds of surfaces, which will be further discussed below.

The cross section profiles of part of the surfaces are extracted, as shown in Fig. 3. The locations of the cross sections are indicated in Fig. 2. Fig. 3(a) shows the cross-section profile of *P. serrulata*. One can hardly identify the boundary between two microstructures without comparing with Fig. 2(a), due to the small undulation of the surface. After careful analysis on Figs. 2(a) and 3(a), we find that the surface of the microstructure rises at the boundary, and the ideal model drawn from the cross section profile can be represented by the inset in Fig. 3(a). Compared to *P. serrulata*,

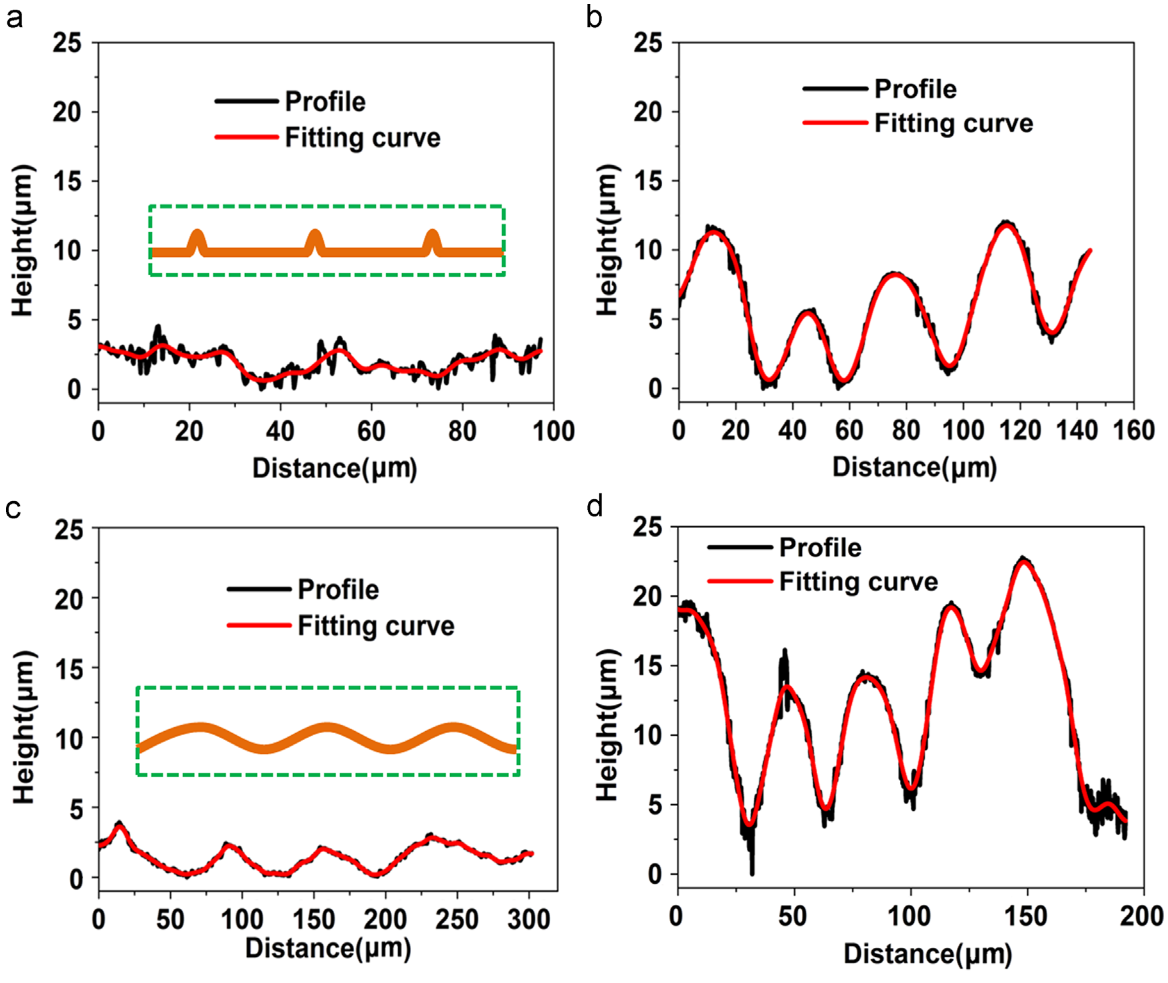

Fig. 3. The cross section profiles of part of the surfaces denoted in Fig. 2(a) *P. serrulata*, (b) Ginkgo, (c) Aloe vera and (d) *H. monogynum*. The smooth red curve guiding for eyes represents the fitting curve of the surface profile. The insets in (a) and (c) indicate the two kinds of surface models, respectively.

the surfaces and microstructures of Ginkgo, Aloe vera and *H. monogynum* are quite different. The surfaces undulate relatively larger and the profile of microstructures can be clearly observed. These three profiles corrugate like the sinusoid, so the shape of the profiles can approximately be considered as sinusoidal shape, as the model shown in the inset in Fig. 3(c). The two kinds of models shown in the insets of Fig. 3(a) and (c) exhibit distinct wettability.

Two classical models, the Wenzel model and Cassie model [4], elaborate the phenomena of a water droplet on a rough surface. In the Wenzel state, the liquid penetrates into the grooves of the surface structures, which makes the hydrophilic surface more hydrophilic and the hydrophobic surface more hydrophobic. The contact between a water droplet and the model in the inset of Fig. 3(a) can be regarded as the Wenzel state. A water droplet diffuses easier on the relatively flatter surface, leading to a relatively smaller contact angle. The raised boundary interacting with the droplet may further decrease the contact angle, as the Wenzel model illustrates. These are the main reasons for the smallest contact angle in *P. serrulata*. Unlike in the Wenzel model, the contact between a water droplet and surface in the Cassie model is more complicated, as air may be trapped in the grooves by water [4]. This makes the contact area between the water droplet and surface smaller and hence causes the contact angle generally larger, compared with the Wenzel model. The Cassie state may dominate the wetting states of a water droplet on the surface indicated by the model in the inset in Fig. 3(c). That is, Ginkgo, Aloe vera and *H. monogynum* exhibit different wetting state from *P. serrulata*, as shown in Fig. 3(b), (c) and (d). So they possess relatively larger contact angle. But it is still a little confusing that Ginkgo exhibits small contact angle, merely 63.01°, though its surface corrugates like the model in the inset in Fig. 3(c).

Fig. 3 showing the cross section profiles only display the two-dimensional structures of the surfaces, which may not explain the wettability involving the three-dimensional structures quite well in the case like Ginkgo. The structural differences between Ginkgo surface and the other three kinds of surfaces can be seen in Fig. 2. The microstructures on the Ginkgo surface generally appear to be long and narrow, and are kind of aligned, compared to the staggered distribution of the other three kinds of microstructures. The grooves formed between the microstructures at this situation facilitate the diffusion of the water droplet on the surface, which therefore leads to a small contact angle on the Ginkgo leaf surface, though it possesses similar cross section profile shape with that of Aloe vera and *H. monogynum*.

More detailed information on the surface microstructures, such as the average distance between adjacent peaks D, the average peak height H obtained from Fig. 3, are shown in Table 1. Moreover we choose ten microstructures on each kind of leaf surface randomly, and then calculate the average length and width of the microstructures, as included in Table 1. *P. serrulata* has the smallest peak height, merely 0.91 μm, confirming the aforementioned small undulation of its leaf surface, which together with the raising edges between microstructures make the surface wettable. The shape of the four kinds of surface microstructures is approximately signified by the average length and the ratio between the average length and width. The ratio L/W of the microstructure on Ginkgo leaf surface is 3.68, about two to three times that of the other three kinds of leaf surfaces. And the microstructures of Ginkgo leaf surface are generally long and aligned, which as stated previously causes small contact angle on the Ginkgo leaf surface. Little difference exits between the ratios L/W of Aloe vera and *H. monogynum*, so the difference of the microstructures shape may be not the main reason for the distinction of the wettability of the two leaf surfaces. The evident differences between Aloe vera and *H. monogynum* are the height and spacing (pitch value) of the microstructures on the leaf surfaces. The height of the microstructure on the Aloe vera leaf surface is about 2.0 μm, less than one fourth of that of *H. monogynum*, as shown in Table 1. And the pitch value is 72.62 μm, more than two times that of *H. monogynum*. So the microstructures on Aloe vera leaf surface exhibit large pitch value and small height, which affects the contact state between a water droplet and surface [19]. Water may impregnate between microstructures, entering the Cassie impregnating wetting state [20], where the contact area between water and surface is less than that of the Wenzel state and larger than that of the Cassie state. The microstructures with small pitch value and large height on the *H. monogynum* leaf surface may keep the water droplet out of the grooves, thus reducing the liquid–solid contact area and improving the nonwettability. That is, the ratio between the height and pitch value of the microstructures (H/D) plays an important role in the wettability of surface to some extent. The ratio H/D of Aloe vera is about 0.028, nearly one ninth that of Aloe vera, leads to the relatively smaller contact angle. The ratio H/D of Ginkgo is 0.2, about seven times that of Aloe vera. So from this point, Ginkgo could show better nonwettability except for the approximately linear distribution of the microstructures.

Table 1
The average distance between adjacent peaks D, the average peak height H obtained from Fig. 3. The average length L, width W and the ratio between them L/W of the microstructures.

Surfaces	D (μm)	H (μm)	L (μm)	W (μm)	L/W
Photinia serrulata	19.17	0.91	26.49	19.04	1.41
Ginkgo	34.42	6.94	77.68	22.40	3.68
Aloe vera	72.62	2.00	64.19	52.50	1.22
Hypericum monogynum	33.86	8.96	35.68	24.61	1.48

As discussed above, we focus on the effects of microstructures on the surface wettability. In fact, the nanostructures may also affect the contact angles of the surfaces. Multiscale structures are reported to be important for the superhydrophobicity of surface [21]. But researchers believe that the nanostructures per se are beneficial but not essential for the superhydrophobicity [22]. As shown in Figs. 2 and 3, nanostructures can also be observed on the four kinds of leaf surfaces. They may reduce the liquid–solid contact area since water can hardly impregnate grooves at the nanoscale, thus modifying the surface wettability. Even so, the microstructures could be the key impact factor of wettability.

4. Conclusions

We investigate the wettability of the leaf surfaces of four kinds of plants, *P. serrulata*, Ginkgo, Aloe vera and *H. monogynum*, by comparing the static contact angle. *P. serrulata* leaf surface has the smallest contact angle, 60.43°, showing hydrophilicity, while that of *H. monogynum* leaf surface exhibits the largest contact angle. And the Aloe vera and Ginkgo leaf surfaces take the second and third places respectively. The differences of the surface microstructures account for the distinction of wettability. The small corrugation and raised boundary of the microstructures make *P. serrulata* to be the most wettable surface of the four kinds of plant leaf surfaces. Corrugated cross section profile reduces the contact area between liquid and surface and hence is beneficial for the surface nonwettability. Ginkgo shows corrugated microstructures on the leaf surface, but they have large ratio of *L/W* and are well aligned, which facilitates the diffusion of liquid, thus causing the Ginkgo leaf surface hydrophilic. Further investigation shows, compared to Aloe vera leaf surface, that of *H. monogynum* exhibits large height and small pitch value of the microstructures, leading to the relatively larger contact angle. The analysis in this work explains the effects of microstructures on the wettability of leaf surfaces, which advances our understanding of surface wettability and also shed light on the bionic design of surfaces for different wettable needs.

Acknowledgments

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