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Investigation on hydrophobicity of lotus leaf: Experiment and theory

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ABSTRACT

A detail experiment investigation on hydrophobicity of lotus leaf had been given, including contact angle, entrapped gas, micrometer and nanometer surface topographies. Four kinds of lotus leaf surfaces were involved: fresh front (FF), dried front (DF), fresh back (FB) and dried back (DB) surfaces. The basic mechanisms of the liquid spreading on a rough surface and the entrapped gas under a drop had been discussed. Based on the mechanisms and experiment, hydrophobicity of the four lotus leaf surfaces was analyzed. The investigation results showed that the hydrophobicity of the front surfaces was dominated by the entrapped gas under the drop and the absolute stable position of the contact line while the back surfaces by metastable positions of the contact line, resulting in the ultrahydrophobicity on the front surfaces and large contact angle hysteresis on the back surfaces. The effects of dual-size surface structures on the hydrophobicity were discussed in detail. Because the nano-pillars were firmly close together, there was no entrapped gas in the nano-structure on the front surfaces. The structure of micro-pillars was a main cause for the ultrahydrophobicity of the front surfaces. However, on the FB surface, the structure of nano-pillars was a main cause to induce entrapped gas.

1. Introduction

Ultrahydrophobic surfaces should have a large static contact angle and a small contact angle hysteresis (the difference between advancing and receding contact angle) [1,2]. Ultrahydrophobicity of many plant leaves, notably the lotus leaf, has recently gained much attention because of the self-cleaning characteristics [3–7]. A surface's hydrophobicity is mainly determined by the chemical composition and the topography of the surface [3]. All primary surfaces of plant leaves are composed of a mixture of hydrophobic compounds called "waxes" [8,9]. Because water contact angles on smooth hydrophobic surfaces are rarely higher than 120° [10], the ultrahydrophobicity is primarily induced by surface micro/nano-structures. The surface structures of natural plant leaves are diverse, therefore a lot of leaves have been investigated [4,11–13]. However based on the hydrophobic mechanism, there are two kinds of typical hydrophobic surfaces: one is ultrahydrophobic surface characterized by a large advancing contact angle but a small hysteresis [11,12]; and another is a surface characterized by a large advancing contact angle and a large hysteresis or high adhesive force [13], which is mainly induced by the metastable position of the contact line (MPCL). In order to discuss conveniently later, the second surface is called MPCL surface here. The lotus leaf is firstly concerned because of the ultrahydrophobicity of its front surface, while its back surface is a typical MPCL surface. Therefore, the lotus leaf is a typical objective to investigate the basic mechanism of hydrophobicity on diverse plant leaves.

To determine how roughness affects hydrophobicity, Wenzel [14] was the first to develop an equation such as Eq. (1) to discuss the influence of roughness on apparent contact angle. In this equation, an roughness factor f_r is used to relate the contact angles of rough, θ, and smooth surfaces, θ_0.

$$\cos\theta = f_r \cos\theta_0 \quad (1)$$

The roughness factor f_r is defined as the ratio of the true rough surface area to the apparent surface area or the projected area of the rough surface. This equation predicts how to affect the surface hydrophobicity when a water drop on a rough surface spreads and engulfs the surface topography. However, when the true contact angle is larger than $\pi/2$ and gas is entrapped under the drop, Wenzel's formula must be modified. Cassie and Baxter [15] extended Wenzel's equation for this composite solid–liquid–gas interface. In order to calculate the contact angle for the composite interface, the equation is given by

$$\cos\theta = f_r f_{sl} \cos\theta_0 + f_{sl} - 1 \quad (2)$$

where f_{sl} is fractional flat geometrical area of the solid–liquid under the drop; f_r is the roughness factor for the solid–liquid interface. This equation shows the area of liquid–gas interface under the droplet on the apparent contact angle. According to Eq. (2), the entrapped gas under a drop is a key for surface ultrahydropho-

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bicity. For entrapped gas in the microstructure under the drop, some criteria have been proposed [16–19].

The surface hydrophobic states induced by the entrapped gas have been discussed recently [20–23]. However, when the fractional area of the solid–liquid interface is large enough, the position of the contact line also can induce a metastable state and affect the contact angle and its hysteresis greatly [24]. When a liquid spreads on a rough surface so as to cover an arbitrary domain, contact line continues to move until it arrives at an equilibrium position of minimum total surface energy. But it need not necessarily be the absolute minimum, and subsidiary minimum, as well as the absolute minimum, can exist so that metastable positions of the contact line as well as absolute stable equilibrium are possible [24]. For the complexity of the real surface topography, the range of Wenzel and Cassie equations applicability has being discussed recently [25–27]. No matter what discussion, Wenzel and Cassie equations are mainly applied to evaluate the effect of the interface between the drop and the solid on the contact angle. When the liquid spreading is dominated by the metastable positions of the contact line, Wenzel and Cassie formulas only can give the general direction of the liquid surface not too near the solid, and the shape of the liquid surface in the immediate vicinity of the solid must be upon the particular form which the roughness takes [24]. When the contact angle is up to the metastable positions of the contact line, an apparent characteristic is a large hysteresis [17,24]. Therefore, the liquid spreading on the MPCL hydrophobic surface should be dominated by metastable positions of contact line.

In this paper, objectives of the investigation involved fresh front (FF), fresh back (FB), dried front (DF) and dried black (DB) lotus leaf surfaces, which showed two typical kinds of the liquid spreading on three typical kinds of rough surfaces. The tasks of the paper were to investigate hydrophobicity of the different lotus leaf surfaces and explore their hydrophobic mechanisms.

2. Experiment

2.1. Sample preparation

For this study, fresh and dried lotus leaves were selected. Lotus leaves were obtained from a lotus pool in Tsinghua University. In nature, plant leaves always get contaminated with various particles. Each leaf was rinsed under running water, which would remove some contaminants without damage of surface wax and structure. In order to preserve the quality of fresh leaves, each leaf was hold integratively and its trunk was immersed in water before experiment. Experiment for fresh lotus leaves was finished in one day since they had been obtained from the pool. Dried leaves were obtained through nature evaporation of more than three days. In experiment, 30 mm × 30 mm was cut from the leaf between the veins, and was placed on the measuring platform and attached using double sided tape. For fresh leaves, experiment was rapidly finished as soon as possible after being cut to reduce the effect of shrinking induced by evaporation.

2.2. Contact angle

Contact angle was measured on a home-built contact angle analyzer, which basic principle is similar with one from Kwok and Neumann [28]. In order to measure the contact angle precisely, a small hole was drilled at the center of the sample and water was pumped from below the surface. The lotus sample was installed on a tiltable table that was mounted on a moveable table. A motor was employed to drive a syringe to pump water steadily into the drop from below the sample surface. In the experiments, the maximum drop volume was 30 μl, and the increasing and decreasing velocity of the drop volume was near 1 μl/s. Table 1 shows contact angles on different surfaces. In the table, each data was a mean from four different samples. The advancing contact angles were similar on the different surfaces. The contact angle hysteresises were distinctly smaller on front surfaces than on the back surfaces. The contact angle hysteresises were also smaller a little on fresh surfaces than on the dried surfaces. The receding contact angle on DB surface was zero.

Table 1
Contact angles on different lotus leaf surfaces. θ_a, θ_r, and $\Delta\theta$ were apparent advancing, receding contact angles and hysteresis respectively. The sessile drop method was used for water contact angle measurements with a self-developing contact angle analyzer.

	Fresh		Dried	
	Front	Back	Front	Back
θ_a (°)	152	151	151	146
θ_r (°)	130	82	124	0
$\Delta\theta$ (°)	21	69	28	146

2.3. Gas under a drop

Generally ultrahydrophobicity of front lotus leaf surface is due to entrapped gas under a drop. The entrapped gas is a key to affect the hydrophobicity. Here a microscope was employed to observe entrapped gas under a drop. Fig. 1 shows images of the surfaces in air (without a drop) and under a drop. In the figure, gas was at light parts and could be observed clearly on the FF, DF and FB surfaces under a drop. However, there was no gas on the DB surface under a drop, which shows water intruded grooves of the DB surface. When gas existed between the drops and the surfaces, the water–solid and water–gas interfaces could be observed clearly because they were almost at a same height. However, when water intruded the grooves on the surface, only water–solid interface existed. This water–solid interface was at a relative large range of height because of the surface topography, resulting the image of the DB surface under the drop was blurry in (d) because of the effect of the drop on the light route in the microscope. According to Fig. 1, water–gas fractions were distinctly more on the front surfaces than on the FB surface; the water–solid area induced by micrometer pillars was larger a little on the FF surface than on the DF surface. At the same time, nonuniform gas distribution could be observed on the surfaces because of the nonuniform surface structures induced by the growth in nature.

2.4. Surface topography

Hydrophobicity of lotus leaf is due to a layer of hydrophobic wax on the surface and a typical dual-scale structure surface topography. To investigate micrometer scale surface topography, an optical profiler of MicroXAM from ADE Corporation was used for characterization of the surface topographies. A 50× objective was used with scan size of 173 μm × 128 μm and lateral resolution of 0.5 μm. Four different surface height maps and 2D profiles can be seen for the different lotus leaf surfaces in Fig. 2. In each figure, a 3D map and a flat map along with a 2D profile in a given location of the flat 3D map are shown. In Fig. 2, it is clear that the front surface profiles were similar and they were different with the back surfaces. There were a lot of micro-pillars distributed randomly on the front surfaces. The average periodic distance and height of the micro-pillars were 20 μm and 15 μm respectively. The peaks of the micro-pillars were approximately half spheres with about 7 μm diameter. Due to shrinking, the peaks inclined to be flat and the side slopes became larger on the DF surface. The topography of the FB surface was constructed by irregular micro-bumps, which arranged close together. The average curvature radius of micro-bump peaks was