

Stability of Superhydrophobicity of Lotus Leaf under Extreme Humidity

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We systematically evaluated water contact and sliding angles on the lotus leaf from -10 to 80 °C under either extremely low or high relative humidity. SEM images revealed changes of the hierarchical structures after thermal treatment at different temperatures. The wettability recovery test showed consistent results that a restorable loss of superhydrophobic behavior appeared under low temperature and high humidity due to water condensation, whereas structural destruction at high temperatures caused the lotus leaf to lose extraordinary water repellency permanently.

The phenomenon of superhydrophobicity is common in nature.¹ Lotus leaf is usually considered an ideal superhydrophobic surface to exhibit self-cleaning behavior. The micro-/nano-binary structures combining a hydrophobic wax layer on the surface are responsible for this property.² In recent years, many studies have been carried out on water condensation and its effect on superhydrophobic surfaces;^{3–5} however, the results concerning the lotus leaf are somewhat contentious. Several groups reported the least decrease of superhydrophobicity of the lotus leaf by comparing sliding angles of eight plants after condensation at 5 and 20 °C.⁴ In contrast, the wetting transitions from hydrophobic to hydrophilic were also observed via condensing water on lotus leaves in different ways.⁵ The opposite conclusions of condensation effect on the lotus leaf may result from environmental conditions. The microclimate in which the experiment is performed plays a very important role in influencing the stability of superhydrophobicity of lotus leaf.

In previous work,⁶ we designed a humidity chamber inside which the temperature of the sample stage could be precisely regulated by a heated/refrigerated circulator and relative humidity (RH) by adjusting the feeding rate of dry N₂ and water vapor. The chamber was installed on an optical goniometer so that the contact angle (CA) and sliding angle (SA) could be tested in a broad temperature and humidity range. With the aim of clarifying how the superhydrophobic property of the lotus leaf was affected by environmental factors, fresh leaf samples of 1.5×1.5 cm² were cut from similar areas and kept in a refrigerator at 4 °C for testing. After they were attached to the sample stage and then thermally treated for 30 min every 10 °C from -10 to 80 °C under extremely low (RH < 10%) or high humidity (RH > 90%) individually, water droplets of 20 °C were directly syringed to obtain the CA by sessile-drop method. The SA was recorded when the water droplet started to roll away from the leaf surface. The topography of the samples was characterized by field emission scanning electron microscopy. All SEM samples were sputter-coated with 20 nm of gold before observation.

Figure 1 reveals water CA and SA of the lotus leaf measured between -10 and 80 °C under either low or high RH. As seen in Figure 1a, water was not frozen at -10 °C and

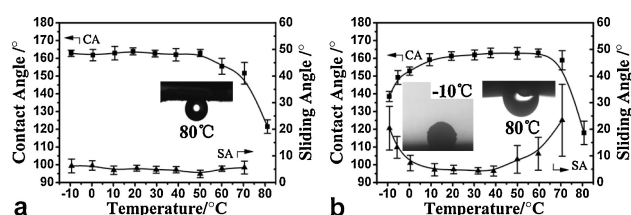


Figure 1. Water CA and SA on the lotus leaf measured between -10 and 80 °C under (a) low RH (<10%) and (b) high RH (>90%).

the CA stably remained at about 162° between -10 and 50 °C under low RH. Outstanding water repellency of the lotus leaf surprisingly existed until -10 °C. This might be attributed to complete hierarchical structures and extremely low humidity. RH < 10% suggested that the dew point was much lower than surface temperature, so water vapor could not be condensed on the leaf surface. However, the CA reduced apparently from 50 to 70 °C, accompanied with a significantly increased measurement deviation in this range. The rapid change of the droplet profile, which was caused by quick water evaporation at high temperatures under low RH, was believed to be the main reason. On the contrary, under high RH (Figure 1b), a water droplet was much easier to solidify as soon as it touched the surface at -10 °C sometimes; therefore, we added to the record of CA values at -5 °C. It was shown that the CA decreased quickly as the surface temperature went below 10 °C. The averaged CA values were $149.2 \pm 3.9^\circ$ at -5 °C and $138.5 \pm 2.9^\circ$ at -10 °C (non freezing). Water condensation on tops of protuberances and in the interspaces between countless nanotubes has been proven to be the leading cause of the loss of superhydrophobicity.⁵ The lotus leaf could keep high CA values of about 162° in the temperature range from 10 to 70 °C. However, with the temperature further increased, the CA sharply dropped down to about 120° at 80 °C under both RH levels. This decline may be in respect of an obvious change of the morphology and chemical composition of the leaf surface.

We also evaluated the water SA under the same condition as the CA test. The SA value depends on the characteristic of the surface and is much sensitive to the substrate.⁷ Under low RH, the SA was maintained around 5° from -10 to 70 °C, demonstrating excellent water repellency. However, when the sample was heated to 80 °C, water droplets could no longer roll away and strongly adhered to the substrate. On the other hand, under high RH, it was only in a much narrower temperature range (from 10 to 40 °C) that the surface displayed a similar low SA. The SA ascended quickly as the temperature went below 10 °C or above 40 °C. In response to the decreased CA values, the SA went up to $20.4 \pm 12.2^\circ$ at -10 °C, confirming loss of

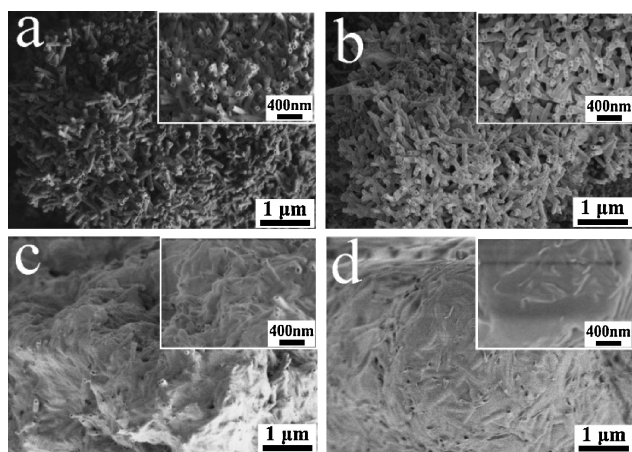


Figure 2. SEM images of the lotus leaf (a) before and after treated at (b) -10 , (c) 70 , and (d) 80 °C for 30 min under RH > 90%.

superhydrophobicity. The same situation appeared at 80 °C. A water droplet became “sticky” to overhang on the surface. Consequently, the lotus leaf lost its superhydrophobicity completely at this temperature.

The change of surface wettability can be confirmed by analyzing the morphology and the interaction energy (Figure S1).⁸ The SEM images of the lotus leaves after thermal treatment at -10 , 70 , and 80 °C under RH > 90% are compared in Figure 2. Figure 2a displayed clear binary structures on the fresh leaf, which consisted of micro-protuberances with the diameter ranging from 5 to 10 μm and numerous nanotubes of 100 – 150 nm vertically assembled all over the surface. No obvious diversity of these hierarchical structures was found between the untreated sample and that treated at -10 °C (Figure 2b). It was demonstrated that water condensation was incapable of causing damage to the surface structure. In spite of that, the change of protuberances could be distinguished apparently at 70 °C (Figure 2c) and all of them collapsed as the sample was heated to 80 °C (Figure 2d), in addition the nanotubes were molten partly at 70 °C and completely at 80 °C. This result proved that the loss of superhydrophobicity would happen under low temperature and high RH or above the temperature of the melting point of the wax layer. The former was closely associated with water condensation, whereas the latter was mainly attributed to the topographic destruction of the surface. Besides, two actions of water under both high temperature and RH must be taken into account to explain that surface damage seemed not to occur at 50 – 70 °C under low RH according to the SA. First, the air trapped in microstructures was easily substituted by water under high RH, causing the increase of SA values. Next, high temperatures accelerated the solution of water-soluble components of the lotus leaf, which might help the wax melting with the presence of water.

To further investigate the loss of superhydrophobicity triggered by condensation or by heating, thermally treated samples under RH > 90% were placed in Petri dishes at room temperature for 24 h, followed by the CA and SA measurements at room temperature under RH of 30%. The results are listed in Table 1. It was shown that the treatment at -10 or 60 °C did not distinctly alter superhydrophobic behavior. However, the CA descended from 159.9 ± 2.3 to 149.9 ± 5.3 ° and the SA

Table 1. Contact and sliding angles (°) for the lotus leaf before and after treatment at -10 , 60 , 70 , and 80 °C

Temperature /°C	Contact angle		Sliding angle	
	Before	After	Before	After
-10	160.2 ± 0.7	160.1 ± 1.1	9.1 ± 2.9	9.2 ± 3.6
60	161.5 ± 3.1	160.5 ± 4.2	10.1 ± 3.6	11.5 ± 4.8
70	159.9 ± 2.3	149.9 ± 5.3	9.9 ± 2.1	17.4 ± 7.5
80	160.6 ± 3.1	133.1 ± 8.7	10.3 ± 2.8	—

ascended from 9.9 ± 2.1 to 17.4 ± 7.5 ° after the treatment at 70 °C, which agreed with the SEM observation in Figure 2c. The structural destruction escalated with further increase of the heating temperature. As a result, the surface recovered from 80 °C became sticky to water droplets, which could not roll away even tilting the surface to 180 °. Correspondingly, the CA went down to 133.1 ± 8.7 °.

In conclusion, we have contrastively studied the stability of superhydrophobicity of the lotus leaf by testing CA and SA under extreme humidity. It was shown that the lotus leaf could hold its highly stable superhydrophobicity in a dry environment (RH < 10%), but the CA descended and the SA ascended on account of water condensation as the temperature fell below 10 °C under RH > 90%, leading to a temporary loss of superhydrophobicity. Fortunately, water repellency was well resumed by placing the sample at room temperature for 24 h. When the leaves were heated higher than the melting point of the wax layer, the loss induced by structural destruction was irreversible. The results indicate that environmental factors, including temperature and humidity, may greatly affect the superhydrophobic property of the lotus leaf. The feasibility of superhydrophobic materials in practical application depends not only on an appropriate architectural design but also on fine adaptability to the environment.

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