Secret of Lotus Leaf: Importance of Double Roughness Structures for Super Water-Repellency

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The physical meaning of double-roughness structure (DRS) surfaces on lotus leaves, which are formed by tens nano-sized and micro-sized structures, is discussed based on the bouncing behavior of water droplets on such surfaces. Super water-repellency and the sliding phenomena of raindrops on lotus leaves are well-known as the “lotus effect”, however, the necessity of the DRS surface has been rarely understood because the lotus effect can be observed on single roughness structure (SRS) surfaces as well. To understand the physical meaning of the DRS surface, bouncing behaviors of water droplets on the lotus leaf were investigated. Two model surfaces that had SRSs and DRSs were prepared from diarylethene (DAE) as a photochromic compound. The SRS surface of DAE, which was covered by random-orientated needle-shaped crystals, showed a non-bouncing behavior. In contrast, the DRS surfaces of DAE and lotus leaves showed bouncing behaviors. The difference between bouncing and non-bouncing behaviors can be elucidated by the Laplace pressure generated by surface structures in comparison with the dynamic pressure generated by the impact of falling water droplets onto the surfaces. The random-orientated needle crystals on the SRS surface generated a smaller Laplace pressure. On the other hand, larger Laplace pressure was generated by some randomly orientated small-sized structures on the large-sized structures of the DRS surfaces of DAE and lotus leaves.

Keywords: Super water-repellency, Lotus effect, Double roughness structure surface, Laplace pressure

1. Introduction
A lotus leaf completely repels raindrops (Fig. 1a) that roll down on a slightly tilted lotus leaf. This phenomenon is called the lotus effect [1-5], and is one of the most important topics in biomimetics. In current studies of wetting phenomena, the lotus effect is explained by the double roughness structure (DRS) surface on lotus leaves. Here, the DRS surface is defined as the surface that is covered by both large-sized and small-sized structures, wherein the large-sized structures are further covered by small-sized ones, as shown in Fig. 1b. The lotus effect includes two aspects: super water-repellency (contact angle $\theta \geq 150^\circ$) and the sliding phenomena of water droplets on slightly tilted lotus leaves. Here, we focused on the bouncing behaviors of raindrops on a lotus leaf, as shown in Fig. 1b. The mechanism on the basis of DRS surfaces is rarely understood as follows.

The super water-repellency of the lotus effect is frequently explained by the Cassie–Baxter state (Fig. 2) [5-7]: a water droplet touches only the heads of pillars along the normal direction and does not penetrate the spaces between them. As a result, air occupies this space between the pillars. The contact angle in the Cassie–Baxter state, $\theta_{CB}$, is described by Eq. (1):

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2,$$  \hspace{1cm} (1)

where $f_1$ and $f_2$ are area fractions of Species 1 and 2, respectively; $f_1 + f_2 = 1$; and $\theta_1$ and $\theta_2$ are contact angles of Species 1 and 2, respectively. In other words, $\theta_{CB}$ is the contact angle for the mixed surface of Species 1 and 2. If Species 1 and 2 are the hydrophobic material and air, respectively, we then
obtain Eq. (2) for the mixed surface of Species 1 and air from Eq. (1) [5-7]:

$$\cos \theta_{CB} = f_1 (1 + \cos \theta_1) - 1 \quad (2)$$

Actually, we can see the shining surface under water droplets on a lotus leaf due to the reflection of sunlight from the air–water interface, as shown in Fig. 2. The Cassie–Baxter state occurs on the single roughness structure (SRS) as well as on DRS surfaces.

On the other hand, sliding phenomena on a lotus leaf is explained by the local pinning effect by small-sized structures on large-sized structures, as shown in Fig. 3 [8,9]. Generally, the pinning effect means that the contact line of a water droplet is pinned by pinning points such as surface structures (physical defects) and contaminants (chemical defects) [6,10] and that the surface area of the pinned droplet increases due to its deformation, which corresponds to pinning energy [10]. Subsequently, a droplet slides down when its potential energy between two large-sized structures on a lotus leaf becomes larger than the local pinning energy by small-sized structures.

The super water-repellency induced by the Cassie–Baxter state and the sliding phenomena can be explained on the basis of the DRSs on the surface. However, the lotus effect and bouncing phenomena can be observed on SRS surfaces as well (multi-pillar surface), as shown in Fig. 2 [11]. This result means that the DRS is not always required to generate the lotus effect. Therefore, it is very difficult to find an answer to the fundamental question as to why a lotus leaf forms a DRS on its surface. The essence of the answer is presented here as an extension of our previous study [12].

2. Theory of Laplace pressure and dynamic pressure

There are two factors to understanding the bouncing phenomena [11]. One is the Laplace pressure $P_L$ generated by surface structure due to the curvature ($R$: curvature radius) of the air–water interface among surface structures as shown in Fig. 4. Considering a multi-pillar surface with pillar height $h$, pillar diameter $D$, and pillar pitch $p$ in square lattice, $P_L$ is described by Eq. (3) [11]:

$$P_L = 2\gamma/L \approx 16\gamma H/(p\sqrt{2} - D)^2. \quad (3)$$

Equation (3) is valid under the condition of $p >$
$H$. $P_L$ is the minimum pressure to penetrate, determined by the characteristic scales of surface structures.

The other factor is dynamic pressure $P_d$, generated by the impact of a falling water droplet against the surface. $P_d$ is expressed by Eq. (4) [12]:

$$P_d = \left( \frac{1}{2} \right) \rho V^2 = \rho g h,$$

where $\rho$ is density of a falling droplet, $V$ is falling velocity, $g$ is gravitational acceleration, and $h$ is release height. In Eq. (4), the drag force applied to the falling droplet from air is neglected.

The competition between $P_L$ and $P_d$ determines the behavior of a water droplet on the surface [11,12]. If $P_L > P_d$, the water droplet bounces because it cannot penetrate into the space among surface structures. This is more evident when $p$ is quite small. Multi-pillar surfaces, as shown in Figs. 2 and 4, can be classified as SRS surfaces. $P_L$ generated by actual DRS surfaces is discussed below.

3. Bouncing behavior on DRS surfaces and non-bouncing behavior on SRS surfaces of lotus leaves and diarylethene (DAE)

The lotus leaf, which exhibits the bouncing phenomenon for falling raindrops, obviously achieves the condition of $P_L > P_d$. However, the lotus leaf is far from an ideal surface due to the randomness of the arrangement and orientation of surface structures. Therefore, it is required to find criteria to apply Eq. (4) to elucidate the bouncing phenomena on a lotus leaf in comparison with model surfaces. Figure 5 shows schematic representations of the SRS and DRS surfaces prepared using diarylethene (DAE) as well as that of the lotus leaf obtained by SEM observations. DAEs are thermally irreversible photochromic compounds, which show cyclization and cycloreversion reactions by alternative irradiations with UV and visible light (Vis), as shown in Fig. 6 [13-21]. As a result, different DAE crystals with different lattice constants were formed due to the difference in structures [17]. This point is very important to prepare the needle-shaped and rod-shaped crystals on SRS and DRS surfaces as shown in Fig. 5 by alternating UV/Vis irradiation, storage temperature, and storage time.

Next, modifying non-ideal surfaces into ideal ones in terms of $P_L$ is discussed. On the SRS surface, a non-bouncing behavior was experimentally
observed when we released water droplets from a 2-mm height \( (P_d = 17.6 \text{ Pa}) \). The SRS surface was covered by needle-shaped crystals of 1c, and the crystals almost lay on the surface, as shown in Fig. 5a, implying that there were no needle-shaped crystals along the normal direction corresponding to the pillars as shown in Fig. 4. From typical SEM images of the SRS surface of DAE, the values of \( p \), \( H \), and \( D \) were estimated to be \( > 500 \), 7.6, and 1 \( \mu \text{m} \), respectively, as shown in Fig. 7a. In particular, it was impossible to find needle-shaped crystals along the normal direction in SEM images. As a result, \( P_L \) was estimated to be smaller than \( P_d \) (17.6 \( \text{ Pa} \)) using Eq. (3). In other words, \( p \) in Eq. (3) was quite large and \( P_L \) was quite low.

On contrary, a bouncing behavior was observed on the DRS surface when we released water droplets from a 10-cm height \( (P_d = 980 \text{ Pa}) \). This surface was covered by needle-shaped crystals and the rod-shaped crystals were covered by the needle-shaped crystals as shown in Fig. 5b. The needle-shaped crystals were observed to lie on the SRS surface. However, the directions of some needle-shaped crystals lying on the side of the rod-shaped crystal were almost along the normal direction as shown by the red arrows in Fig. 5b. This result was found by SEM observations from the side view. Assuming that \( p \) in Eq. (3) corresponds to the average interval between the rod-shaped crystals, it is possible to estimate \( P_L \) of the DRS surface. From typical SEM images of the DRS surface of DAE, the values of \( p \), \( H \), and \( D \) were estimated to be 35, 3, 0.2 \( \mu \text{m} \), respectively, as shown in Fig. 7b. As a result, Eq. (3) can be modified to Eq. (5):

\[
P_L = 16 \gamma H_{\text{small}} / (p_{\text{large}} \sqrt{2} - D_{\text{small}})^2,
\]

where \( H_{\text{small}} \) is the average height of the smaller-sized structures along the normal direction, \( p_{\text{large}} \) is the average pitch between large-sized structures and \( D_{\text{small}} \) is the average width of the small-sized structure. In other words, these characteristic scales of the DRS surface are included in Eq. (5). \( P_L \) was estimated to be 1400 Pa using Eq. (5). Therefore, the condition of the bouncing behavior, \( P_L \) (1400 Pa) > \( P_d \) (980 Pa), can be explained. On the other hand, non-bouncing behavior was observed when water droplets were released from a 15-cm height \( (P_d = 1470 \text{ Pa}) \). The condition of the non-bouncing behavior, \( P_L \) (1400 Pa) < \( P_d \) (1470 Pa), was explained. Therefore, it was confirmed that the correlation between \( P_L \) and \( P_d \) can explain bouncing/non-bouncing behaviors on DRS surfaces using Eq. (5).

It is necessary to compare the \( P_L \)s of DAE surfaces to those of lotus leaves to check the validity of the bouncing behavior on the DRS surfaces. In addition to the above scenario, the small-sized structures along the normal direction are important as shown in Fig. 5c and \( p \) was evaluated from the average interval between the large-sized structures. From the SEM images of the lotus leaf, \( p \), \( H \), and \( D \) were estimated to be 20, 1.7, and 0.03 \( \mu \text{m} \), respectively, as shown in Fig. 7c. Using Eq. (5), \( P_L \) of the lotus leaf was estimated to be 2500 Pa. In our experiments, the bouncing behavior was observed on the lotus leaf even when the water droplets were released from a 15-cm height \( (P_d = 1470 \text{ Pa}) \). The condition of the bouncing behavior, \( P_L \) (2500 Pa) > \( P_d \) (1470), was confirmed. Table 1 summarizes the values of \( p \), \( H \), \( D \), and \( P_L \) of the SRS and DRS surfaces of DAE and the lotus leaf.

### Table 1. Characteristic scales and \( P_L \) of single roughness and double roughness structure surface of DAE and that of the lotus leaf.

| Surface                  | \( p \) (\( \mu \text{m} \)) | \( H \) (\( \mu \text{m} \)) | \( D \) (\( \mu \text{m} \)) | \( P_L \) (Pa) |
|--------------------------|------------------------------|------------------------------|------------------------------|----------------|
| Single-roughness DAE     | > 500                        | 7.6                          | 1                            | < 17.6         |
| Double-roughness DAE     | 35                           | 3                            | 0.2                          | 1400           |
| Lotus leaf               | 20                           | 1.7                          | 0.03                         | 2500           |

4. Physical meaning of larger-sized structure in DRS surface

Based on the above discussion, we considered the role of the large-sized structures in the DRS surface. Figure 7 shows schematic representations of water droplets on SRS and DRS surfaces of DAE and that of the lotus leaf. In principle, SRS surface showed bouncing phenomena if the arrangement of surface structure was prepared precisely [11]. Therefore, the DRS surface is not always required. However, the randomly orientated small-sized structures cannot induce the function of bouncing, as shown in Fig. 7a, because suitable \( p \) cannot be obtained in Eq. (5) by the randomized orientation.

On the other hand, the large-sized structure on the DRS surface on DAE surface and the lotus leaf eliminated the effect of the random orientation of small-sized structures, because some small-sized structures on the side of large-sized structures were orientated along the normal direction as shown in Fig. 7b and suitable \( p \) can be set. This is the physical meaning of the large-sized structure of the DRS surface. In other words, precisely periodic structures are not always required in the preparation of DRS
surfaces to design the lotus effect.

Here, we discussed the bouncing phenomena based on the conditions of $P_L > P_d$ accomplished by the DRS surfaces. This scenario is helpful to understand why the Cassie–Baxter state easily occurs on a lotus leaf. The condition of $P_L > P_d$ is very important in wetting phenomena.

5. Conclusion

The bouncing behaviors of water droplets on SRS and DRS surfaces of DAE and a lotus leaf were discussed in terms of $P_L$ and $P_d$. On the SRS surface, the observed non-bouncing phenomena is explained by a quite low $P_L$, because the orientation of the needle-shaped crystals on the surface was random. However, the bouncing behavior was observed on the DRS surface although the orientation of the needle-shaped crystals was random. This is understood by the mechanism that the large-sized structures on the DRS surface play a role to change the direction of some needle-shaped structures to the normal direction. As a result, these needle-shape crystals generated large $P_L$, and induced the bouncing phenomena. Obviously, the DRS surface eliminated the effect of the randomly orientated smaller-sized structures by the large-sized structures. The same scenario can explain the behavior on the lotus leaf. These findings allow us to design the functions of the lotus effect and the bouncing ability by DRS surfaces.

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