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Understanding superhydrophobic behaviors on hydrophilic materials: a thermodynamic approach

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Abstract

Some experiments have proved that superhydrophobic behaviors can be achieved on inherently hydrophilic substrates without low surface energy modification at micro-scale. However, the thermodynamic mechanisms about these results have not been well-understood. In this work, a 2D analytical model was reported to analyze this unexpected experimental observations and wetting behaviors on trapezoidal, vertical and inverse-trapezoidal microstructure surfaces. Theoretical results showed that intrinsic contact angle, which was restricted by sidewall angle of micropillars, was not an independent parameter to affect superhydrophobicity. And re-entrant structures were critical in the realization of microstructures alone inducing transition from hydrophilicity to superhydrophobicity. The wetting transition criterion was that sidewall angle should be less than intrinsic contact angle. On this occasion, a positive energy barrier could support liquid/vapor interfaces and separate Wenzel and Cassie state on hydrophilic substrates. And the physical explanations can be found that the positive energy barrier mainly came from the growth of the high-energetic solid/vapor interfaces to be wetted by the drop with liquid/vapor interfaces moving down inverse-trapezoidal pillars. As for the optimal design of microstructures, considering the limitation of pillar width and the ‘sag’ transition caused by pillar height, T-shape microstructures could be a good choice.

1. Introduction

Superhydrophobic surfaces (contact angle higher than 150°, sliding angle lower than 10°) have been studied extensively due to its potential application, such as anti-icing [1, 2], oil/water separation [3, 4], corrosion resistance [5, 6] and antibacterial coatings [7, 8]. From wetting mechanism perspectives, the forming of superhydrophobic states mainly depends on the micro- or nanotexture and surface chemistry [9]. According to the Wenzel’s equation, a rough surface can make hydrophilic substrates become more hydrophilic and hydrophobic substrates become more hydrophobic [10]. So superhydrophobic surfaces are always prepared on hydrophobic materials or to reduce surface energy on rough hydrophilic surfaces by some organic materials [11]. However, the durability of organic materials is always poor, which limits the application of superhydrophobic coatings, especially in harsh environment [12, 13]. Therefore, superhydrophobic coatings prepared on inorganic materials, which intrinsic contact angle is always less than 90°, could be very promising.

Recently, some reports have shown that superhydrophobicity can also be acquired on inherently hydrophilic substrates without low surface energy modification. For example, Otten et al have found that a water droplet can be held by hydrophilic hairs on the leaves of Lady’s Mantle [14]. Cheng et al also have proved that the wax on lotus leaves is hydrophilic and the contact angle is about 74°, rather than the expected hydrophobic material [15]. Apart from leaves of natural plant, some artificial superhydrophobic surfaces have been prepared on some hydrophilic materials without low surface energy modification [12, 16–21].

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As for the preparation methods, there are two approaches to achieve hydrophobicity on inherently hydrophilic substrates. One is to make hydrophilic substrates with cavities and the trapped air in cavities can inhibit the liquid from wetting the surface. Abdel salam et al have proved that the contact angle of gold surfaces can be larger than 130° if the substrates are decorated with 400–800 nm pores [16]. Ems et al also have achieved the transition from hydrophilicity to hydrophobicity on silicon substrates with cavities which intrinsic contact angle is less than 45° [18]. The other one is to prepare re-entrant or overhang structures on substrates [22, 23]. Cao et al show that overhang micro-textures can induce superhydrophobic behaviors on Si substrates which intrinsic contact angle is 74° [17]. And similar microstructures are also applied to prepare robust omniphobic surfaces, which mechanism is perfectly consistent [24]. Wang et al [21] and Yang et al [12] have proved that T-shape microstructures can induce superhydrophobic behaviors on hydrophilic surface without any organic modification.

Apart from contact angle, sliding angle is also a very important parameter for superhydrophobic surfaces, especially for self-cleaning and drag reduction [25–27]. Although hydrophilic substrates with cavities can perform a high contact angle, air pockets could be sealed in cavities and the surface could become high adhesive due to the forming of the ‘Gecko’ state [28]. Therefore, the re-entrant or overhang structures superhydrophobic surfaces should deserve some more studies, since air pockets are open to the atmosphere. As for the mechanism about re-entrant structures inducing superhydrophobicity, local surface curvature, the third parameter to affect superhydrophobicity, could be a very important factor [24, 29]. Due to locally valid Young’s equation near overhang pillars, three-phase contact line can move upward under the effect of surface tension, which can support Cassie state on hydrophilic materials [17, 24]. However, these explanations and discussions about local surface curvatures are qualitative. Some quantitative thermodynamic analysis and analytical correlation about overhang structures and superhydrophobicity on hydrophilic substrates is still essential. It is helpful to design and optimize surface microstructures to get a more stable superhydrophobicity.

In this paper, we mainly focused on the overhang micro-structures superhydrophobic surfaces, and a 2D analytical model was proposed to describe and analyze surface wetting states. The thermodynamic mechanism that overhang structures could induce superhydrophobicity on hydrophilic substrates was studied quantitatively. And the effects of topographical features on superhydrophobic behaviors were analyzed in detail. Some analysis about optimal geometry were also presented according to thermodynamic calculations.

2. Thermodynamic model

The process of a drop wetting rough substrates can be considered as the wetting transition from Cassie state to Wenzel state. When the pillar height is relatively high, liquid/vapor interfaces will move down pillars gradually, and intermediate wetting state will appear [30–32]. In order to describe the detailed evolution of free energy with liquid/vapor interfaces descending, a 2D thermodynamic model about unit height free energy barriers (UHFEB) was proposed to analyze wetting states of droplets on superhydrophobic surfaces and to clarify the mechanism about a stable liquid/vapor interfaces on hydrophilic rough surfaces. To simplify the problem and derive analytic expressions about UHFEB, some assumptions about thermodynamic analysis were followed as [33]: (1) the drop was spherical; (2) line tension and gravity were ignored; (3) the liquid/vapor interfaces between the pillars were flat; (4) the drop size was much larger than the surface microstructures. In terms of thermodynamics analysis, the dimension of pillars is a very important parameter. There are only a few published literatures to report and discuss that overhang structures can induce superhydrophobicity on hydrophilic substrates without low surface energy modification [14, 17, 21, 29]. And the dimension of micro-textures in these literatures mainly focus on microscale. Although hierarchical textures always get more attention in surface science, we mainly focus on dimension of the pillars at micro-scale, rather than sub-microscale or nanoscale.

The schematic of 2D surface geometry with a drop was shown in figure 1. There were three different pillar-textured surfaces selected in this study: inverse-trapezoidal pillars, vertical pillars and trapezoidal pillars. And sidewall angle α, pillar height H, pillar width a, and pillar spacing b were shown in figure 1(a). If a water drop exhibited Cassie state, the apparent contact angle of the drop could be determined by Cassie’s equation [34]:

\[
\cos \theta^c_s = f \cos \theta_Y + f - 1
\]  

where \(f\) was the solid/liquid region fraction and \(\theta_Y\) was intrinsic contact angle. When the liquid/vapor interfaces moved down the pillars, the intermediate state would form, and the penetration depth of the drop was defined \(h\) (figure 1(c)). Because the drop was spherical, the drop length \(L_k\) equaled \(R \sin \theta^c_s\), where \(R\) was radius and \(\theta^c_s\) was the apparent contact angle when the penetration depth was \(h\) (figures 1(b) and (c)). And the number of micro-pillars contacted with the drop was written as:

\[
n = (2L_k + b)/(a + b)
\]
As for superhydrophobic surfaces with vertical pillars, the volume of the drop should be constant during the wetting transition process. And the external part of the drop above the top of the pillars could be also considered as spherical type. So the geometrical equation of the drop could be written as equation (3):

$$\theta^o_k \frac{L_k^2}{\sin^2 \theta^o_k} - L_k \cot \theta^o_k = \theta^b_k \frac{L_k^2}{\sin^2 \theta^b_k} - L_k \cot \theta^b_k + (n - 1)bh$$

To analyze wetting transitions from Cassie to Wenzel state, the free energy change was derived in the process of liquid/vapor interfaces moving down. When the penetration depth of the drop was $h$ (figure 1(c)), the free energy of the system could be represented as

$$E^h = \gamma_{SV} L_{SV}^h + \gamma_{SL} L_{SL}^h + \gamma_{LV} L_{LV}^h$$

where $\gamma$ and $L$ represented the interfacial energies and interfaces. The interfaces are distinguished by subscripts SV for solid/vapor interface, SL for solid/liquid interface and LV for liquid/vapor interface. If the liquid/vapor interfaces moved down $\Delta h$, the free energy barriers could be expressed as:

$$\Delta E = E^{h+\Delta h} - E^h = \gamma_{LV} \left( \frac{2 \theta^b_k + \Delta h}{\sin \theta^b_k + \Delta h} \frac{L_k}{\sin \theta^b_k} - \frac{2 \theta^b_k L_k}{\sin \theta^b_k} \right)$$

$$+ 2(\gamma_{SL} - \gamma_{SV})(n - 1)\Delta h$$

So the UHFEB $E_u$ could be defined as the limit of $\Delta E/\Delta h$ as $\Delta h \rightarrow 0$, as shown in equation (6):

$$E_u = \lim_{\Delta h \rightarrow 0} \frac{\Delta E}{\Delta h}$$

Therefore, UHFEB could be regarded as the free energy change when liquid/vapor interfaces moved down per unit height. From equations (5), (6) and Young’s equation (7) [36], UHFEB could be normalized with respect to $\gamma_{LV}$, as shown in equation (8):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_Y$$

$$\frac{E_u}{\gamma_{LV}} = \frac{1}{\gamma_{LV}} \lim_{\Delta h \rightarrow 0} \frac{\Delta E}{\Delta h} = \frac{(1 - n) b \sin \theta^b_k}{L_k} - 2(n - 1) \cos \theta_Y$$

Similarly, for superhydrophobic surfaces with trapezoidal and inverse-trapezoidal pillars, the geometrical equation and normalized UHFEB expression could be expressed as:
One can see that the increasing intrinsic contact angle of materials could bring a higher stability of a composite interface. Therefore, it proved the experimental observation that superhydrophobicity could be induced on hydrophilic surfaces. Figure 2 showed the effect of sidewall angle on normalized UHFEB with different penetration depth \( h \) on hydrophilic materials (\( a = 20 \mu m, b = 20 \mu m, H = 20 \mu m, \theta_v = 85^\circ, S = 10^{-8} m^2 \), where \( S \) was the sectional area of the droplet.).

Through equations (8) and (10), the normalized UHFEB of different surface structures could be calculated numerically. Because the free energy \( (J m^{-1}) \) had been normalized with respect to \( \gamma_{LV}(J m^{-2}) \) in equations (8) and (10), the unit of normalized UHFEB would be meters. Figure 2 showed the typical change of UHFEB curves on hydrophilic surfaces with inverse-trapezoidal pillars, vertical pillars and trapezoidal pillars. It could be seen that the value of normalized UHFEB did not change greatly with different penetration depth, and the normalized UHFEB of different surface structures could be calculated numerically. When the normalized UHFEB was always positive, and the system would prefer Cassie state. It meant that a composite interface could appear on the inverse-trapezoidal microstructure surface. Therefore, it proved the experimental observation that superhydrophobicity could be induced on hydrophilic surfaces.

The critical curve (green curve) about wetting transition could be observed clearly in figure 2(b). When the sidewall angle increased from 83° to 85°, the normalized UHFEB would become negative and wetting transition would start. If \( \alpha \) was larger than the critical value 84.104°, the negative UHFEB curve indicated a fully wetted Cassie state. If an additional energy impact was added to the top of pillars, such as vibration or drop evaporation, the drop would absorb energy from the system and the liquid-vapor interface descending from the top of pillars had to be increased. Although the UHFEB was different with the different penetration depth (figure 2), the stability of Cassie state should mainly depend on \( E_u^0 \). Therefore, \( E_u^0 \) deserved more detailed analysis.

Figure 3 showed the effect of sidewall angle on wetting state on hydrophilic and hydrophobic surfaces. Therefore, it proved the experimental observation that superhydrophobicity could be induced on hydrophilic surfaces.

3. Results and discussion

3.1. Effect of sidewall angle

Through equations (8) and (10), the normalized UHFEB of different surface structures could be calculated numerically. Because the free energy \( (J m^{-1}) \) had been normalized with respect to \( \gamma_{LV}(J m^{-2}) \) in equations (8) and (10), the unit of normalized UHFEB would be meters. Figure 2 showed the typical change of UHFEB curves on hydrophilic surfaces with inverse-trapezoidal pillars, vertical pillars and trapezoidal pillars. It could be seen that the value of normalized UHFEB did not change greatly with different penetration depth, and the normalized UHFEB of different surface structures could be calculated numerically. When the normalized UHFEB was always positive, and the system would prefer Cassie state. It meant that a composite interface could appear on the inverse-trapezoidal microstructure surface. Therefore, it proved the experimental observation that superhydrophobicity could be induced on hydrophilic surfaces.

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Figure 3 showed the effect of sidewall angle on wetting state on hydrophilic and hydrophobic surfaces. One can see that the increasing intrinsic contact angle of materials could bring a higher \( E_u^0 \), regardless of the...
dimensions of the microstructures. It meant that a large intrinsic contact angle was preferred to have a stable superhydrophobicity. The critical value of intrinsic contact angle (the curve intersecting with the \( E_u^0 = 0 \) line) was 70.86° when the sidewall angle was 70°. The positive \( E_u^0 \) indicated that a composite interface could appear if \( \theta_w \) was in the range of 70.86° to 120°. And similar to figure 2, an increasing sidewall angle could decrease \( E_u^0 \). Accordingly, when the sidewall angles increased from 70° to 110°, the critical values of intrinsic contact angle would also increase from 70.86° to 110.97°. It indicated that a small sidewall angle was essential for the forming of Cassie state even if the surface was hydrophobic (the critical value of \( \theta_w \) larger than 90° for green and pink curve in figure 3 due to a large \( \alpha \)). It is in accordance with the previous thermodynamic results about trapezoidal pillars that a critical sidewall angle is necessary for wetting transition [43]. Generally, Wenzel’s equation indicated that a rough surface would become more hydrophilic when substrates were hydrophilic. However, the results in figure 3 showed that intrinsic contact angle, which was restricted by the sidewall angle of rough micro-textures, was not an independent parameter to affect superhydrophobicity. Therefore, it was important to note that sidewall angle, apart from pillar width and spacing, was also very important for microtextures design, especially for superhydrophobicity transition on hydrophilic substrates. Because the shape of local surface curvature mainly depended on the value of sidewall angle, the results in figure 3 also thermodynamically proved that local surface curvature was the third parameter to control wettability [24, 29].

3.2. Effect of pillar width and pillar spacing
Changes in normalized \( E_u^0 \) with respect to sidewall angle \( \alpha \) was shown in figure 4 for different pillar dimensions. Apparently, effect of pillar width and pillar spacing on normalized \( E_u^0 \) were quite similar. From figure 4(a), as pillar width increased from 10 \( \mu m \) to 50 \( \mu m \), the maximum values of normalized \( E_u^0 \) decreased from 10.4 \( m \) to 6.5 \( m \) when the sidewall angle was 70°. And the maximum values of normalized \( E_u^0 \) would also decrease from 15.6 \( m \) to 3.4 \( m \) with the increasing pillar spacing in figure 4(c). These observations implied that the smaller pillar dimensions, the more stable composite interface would be. However, in terms of inducing transition from hydrophilicity to superhydrophobicity, pillar width and pillar spacing had no obvious effect. From the previous thermomechanical analysis, a small sidewall angle was vital to acquire free energy barriers to separate Wenzel state and Cassie state irrespective of solid surface chemistry. But the critical value of sidewall angle (the curve intersecting with the \( E_u^0 = 0 \) line) changed slightly with different pillar width and pillar spacing in figure 4(b) and (d). With pillar width changing, the critical value of sidewall angle ranged from 79.06° to 79.21°, while they were in the 77.62°–79.60° range for different pillar spacing. The change of the critical value were only 0.15° and 1.98° respectively for pillar width and pillar spacing varying in the range of 10 \( \mu m \) to 50 \( \mu m \). In terms of preparing microstructures, the control of sidewall angle with such an accuracy is impossible experimentally. Therefore, effect of pillar width and pillar spacing mainly focused on the stability of superhydrophobic behaviors, but nothing to do with achieving superhydrophobicity from hydrophilic surfaces.

3.3. The criterion for determining cassie state on hydrophilic surfaces
As for wetting transition condition, a strict criterion was that normalized UHFEB should be positive from equations (8) and (10). However, strict analysis and calculation could not be essential and a simpler wetting

Figure 3. Variations of normalized \( E_u^0 \) with respect to intrinsic contact angles for different sidewall angles. (\( a = 20 \mu m, b = 20 \mu m, H = 20 \mu m, S = \times 10^{-6} \mbox{m}^2 \)).
transition criterion could be more practical in terms of the preparation of superhydrophobic surfaces. Apparently, from equation (10), the sidewall angle of pillars must be always less than intrinsic contact angle if a positive $E_u^0$ was expected. Therefore, a simpler criterion could be defined as:

$$\alpha < \theta_Y$$

As for reasonability of this simplified criterion, a very explicit thermodynamic derivation from the viewpoint of free energy was shown, as follows.

Because the volume of water drop was much larger than the surface micro-structures, surface area of spherical cap of the drop could be considered to keep unchanged when liquid/vapor interface moved down slightly. As shown in figure 5, if liquid/vapor interface between two pillars descended $\Delta h$, the change of the free energy could be expressed as:

$$\Delta E = 2 \frac{\Delta h}{\sin \alpha} (\gamma_{SV} - \gamma_{SL}) + 2 \frac{\Delta h}{\tan \alpha} \gamma_{LV}$$

$$= \frac{2 \Delta h}{\cos \theta_Y \sin \alpha} (\cos \alpha - \cos \theta_Y) (\gamma_{SV} - \gamma_{SL})$$

When substrates are hydrophilic, solid/vapor interface tension $\gamma_{SV}$ is larger than solid/liquid interface tension $\gamma_{SL}$. Apparently, if sidewall angle $\alpha$ was less than intrinsic contact angle $\theta_Y$, $\Delta E$ would be positive. It meant that positive energy barriers could appear even if water drops were placed on hydrophilic surfaces with overhang structures. Although water drops wetting hydrophilic surfaces is energetically favorable, the Cassie state could be metastable because extra free energy could be essential to overcome the energy barriers during wetting process [44]. And from equation (12) and figure 5, an explicit physical explanation can be found that the positive energy barriers mainly came from the growth of the high-energetic solid/vapor interface to be wetted by the drop with liquid/vapor interface descending when sidewall angle was smaller than intrinsic contact angle. The criterion of inducing transition from hydrophilicity to superhydrophobicity was $\alpha < \theta_Y$, which was also in accord with the
conclusion analyzed by local surface curvature [24, 29]. And the numerical calculations in figure 3 that the critical values of intrinsic contact angle were slightly larger than sidewall angles also proved this simplified criterion. In terms of experimental results, Cao et al prepared an overhanging structure with sidewall angle 35.3° and 54.7° to achieve superhydrophobicity on Si substrates with intrinsic contact angle 74° [17], which were also compatible with our theoretical analysis.

Although the theoretical criterion was $\alpha < \theta_Y$, sidewall angle should be much smaller than intrinsic contact angle in terms of preparing superhydrophobic surfaces in the experiments. If sidewall angle was slightly smaller than intrinsic contact angle, the energy barrier was also slightly greater than zero from figure 4. Under the effect of temperature, drop impact, vibration or drop evaporation [38, 39, 45, 46], the change of free energy of the drop system could be very likely to overcome energy barriers and Cassie state could not be stable. Therefore, in order to resist the external disturbances and get a robust superhydrophobic surface, sidewall angle $\alpha$ should be as small as possible.

### 3.4. Optimal geometrical design of superhydrophobic surfaces

In order to optimize surface microstructures, more detailed thermodynamic calculations about the relationship among $E_{u0}^n$, surface topography and hydrophobicity of material were shown in figure 6. And the effect of pillar width and pillar spacing was depicted in figure 6(a). It was observed clearly that a small pillar width and spacing were necessary to get a high $E_{u0}^n$, and normalized $E_{u0}^n$ got maximum value 45.57 m when the pillar width and spacing were 1 $\mu$m. It meant that Cassie state could be energetically more favorable with decreasing pillar width and pillar spacing, which was consistent with the experimental results that a wider pillar spacing could be more likely to bring wetting transition [47, 48]. Figure 6(b) shows the results about the effect of intrinsic contact angle and sidewall angle on wetting transitions. One can see that $E_{u0}^n$ would decrease with the decreasing intrinsic contact angle and increasing sidewall angle. When intrinsic contact angle was 120° and sidewall angle was 70°, normalized $E_{u0}^n$ increased to the maximum value 67.9 m. As for surfaces with trapezoid pillars and vertical pillars, the effect of intrinsic contact angle on wetting transitions could be analyzed directly through equations (8) and (10). Apparently, if intrinsic contact angle was less than 90°, UHFEB would be always negative, which would lead
to a fully wetted interface, just as Wenzel’s equation predicted. However, if sidewall angle $\alpha$ was smaller than $90^\circ$, $E_u$ would keep positive even if the intrinsic contact angle was less than $90^\circ$ (the white arrow region in figure 6(b)). Therefore, the air pockets could be trapped beneath the drop on the hydrophilic material when the pillars were inverse-trapezoidal. It was in accord with the experimental results of Cao et al [17].

From the perspective of microstructures optimization, sidewall angle should be as small as possible if superhydrophobic surfaces were prepared on inherently hydrophilic substrates without low surface energy modification. Due to the limitation of pillar width and pillar height, the minimum value of sidewall angle was $\arctan(2H/a)$, as shown in figure 7(a). In order to continue decreasing sidewall angle, one way was to increase pillar width. However, a larger pillar width meant that pillar spacing also had to increase in order to keep a high contact angle in terms of Cassie’s equation. And from figure 6(a), a larger pillar width and pillar spacing had a bad influence on the stability of Cassie state, and an excessive pillar spacing could also bring wetting transition $[48, 49]$. So increasing pillar width may not be a good choice. Another way was to decrease pillar height. But some studies have shown that a proper pillar height is essential for superhydrophobicity $[50, 51]$ and ‘sag’ transition will happen if the pillar height is too low $[52]$. Therefore, in order to keep a proper pillar height and decrease sidewall angle at the same time, mushroom-shape or T-shape pillar microstructures could be a good choice (figure 7(b)). On the one hand, the stem part of mushroom-shape microstructures could provide a relatively high pillar height to avoid ‘sag’ transition. On the other hand, the pileus part could help to decrease sidewall angle and the T-shape pillar microstructures could realize that the sidewall angle became zero, which would help to improve the stability of Cassie state greatly. Therefore, T-shape microstructures should be paid more attention in term of preparation of superhydrophobic surfaces.

Finally, it is noted that a real 3D microstructure should be more suitable for the practical cases and could be beneficial for readers to understand how to affect the outcome in the present work. Nevertheless, here we need to indicate that the present 2D model has been established mainly based on a real 3D microstructure. According to the previous literature $[1]$, a drop parallel to the grooves are considered to simplify the problem, effectively reducing it to a two-dimensional one. Therefore, some conclusions about the effects on superhydrophobicity of pillars width and pillar spacing are consistent with the situation of 3D microstructure. In addition, we also need to note that it is very hard to establish a precise 3D theoretical model, especially, in terms of the mathematical treatments, to describe superhydrophobicity; In contrast, a 2D model is simple and robust, and the conclusions obtained from such a model are reasonable and effective. Moreover, another important issue is the relationship between drop size and microstructure dimension. In the present work, we assume the the drop size is millimeter (about $10^{-3}$m), but much larger than the microstructure dimension (about $10^{-6}$m). Regarding the effects of droplet size on the wetting, and in particular, superhydrophobic behavior, the previous studies have addressed very well, and readers who are interested in may refer to $[53, 54]$.  

Figure 7. Optimal microstructures design of superhydrophobic surfaces. $a$ and $H$ were the parameters of pillar width and pillar height.
4. Conclusions

Based on the proposed analytical model, thermodynamic mechanisms why re-entrant microstructures could induce superhydrophobicity on inherently hydrophilic surfaces have been theoretically analyzed. Results showed that sidewall angle of micropillars played a significant role in superhydrophobicity transition, and the condition for such transition was that sidewall angle should be less than intrinsic contact angle $\theta_i$. The physical explanation was that the growth of the high-energetic solid/vapor interfaces induced by small sidewall angle could provide a positive energy barrier to separate Wenzel and Cassie state when liquid/vapor interfaces descended. As for the microstructure optimization, T-shape microtextures were considered to be a good choice due to a relative high pillar height and small sidewall angle. This structure could provide a high energy barrier and avoid 'sag' transition at the same time, which helped to improve the stability of Cassie state.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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