Supplementary Information

Water super-repellent behavior of semicircular micro/nanostructured surfaces

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1. Theoretical investigations on micro-/nano-semicircular surfaces

It is well known that, the CA of a water droplet on an ideal smooth solid surface can be given by the classical Young's Equation

$$\gamma^{la}\cos\theta_Y = \gamma^{sa} - \gamma^{ls} \tag{1}$$

Where θ_Y is intrinsic CA. γ^{la}, γ^{sa}, and γ^{ls} are the surface tension at liquid-air, solid-air, and liquid-solid interfaces, respectively. The apparent contact angle (θ_{Ww}) of Ww state is given by Wenzel's Equation:

$$\cos\theta_W = r\cos\theta_Y \tag{2}$$

a roughness factor r can be defined:

$$r = r_1 r_2 \tag{3}$$

Where, microtexture factor r_1 can be defined

$$r_1 = \frac{\pi R_1 + b_1}{2R_1 + b_1} \tag{4}$$

Nanotexture factor r_2 can be defined

$$r_2 = \frac{\pi R_2 + b_2}{2R_2 + b_2} \tag{5}$$

For the Cc wetting state, droplets are supported by a composite surface composed of solid and air, the apparent contact angle (θ_{Cc}) can be given by Cassie equation:

$$\cos\theta_{\mathrm{Cc}} = r_f f \cos\theta_Y + f - 1 \tag{6}$$

Roughness ratio of the wet area r_f and the solid fraction f for the 2-D model may be expressed as:

$$r_f = r_{f_1} r_{f_2}$$

(7)

$$f = f_1 f_2$$

(8)

$$r_{f_1} = \frac{\alpha_1}{\sin\alpha_1} \tag{9}$$

$$r_{f_2} = \frac{\alpha_2}{\sin\alpha_2}$$

(10)

$$f_1 = \frac{2R_1 \sin\alpha_1}{2R_1 + b_1}$$

(11)

$$f_2 = \frac{2R_2 \sin\alpha_2}{2R_2 + b_2}$$

(12)

For the simplicity, one can consider the apparent contact angle for Cw wetting state to be equivalent to that of the single structure; only the intrinsic CA is replaced by the Wenzel equilibrium CA on a nanotexture.

$$\cos\theta_{\mathrm{Cw}} = r_{f_1} f_1 r_2 \cos\theta_Y + f_1 - 1 \tag{13}$$

one can also consider the apparent contact angle for Wc wetting state to be equivalent to that of the single structure; only the intrinsic CA is replaced by the Cassie equilibrium CA on a nanotexture.

$$\cos\theta_{\mathrm{Wc}} = r_1 (r_{f_2} f_2 \cos\theta_Y + f_2 - 1) \tag{14}$$

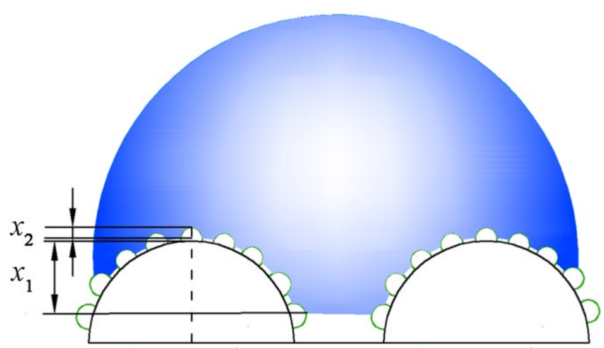

Fig. S1 Illustrate the wetting state of a composite drop on the semi-circular surfaces with micro/ nanoscale hierarchical roughness.

2. The FEB for the transition from one state to the other states

The free energy may be restricted to the total of the interfacial energies, which is written as:

$$F = \gamma^{la} l^{la} + \gamma^{sl} l^{sl} + \gamma^{sa} l^{sa}$$

(15)

Where γ^{ij} are the interfacial energies between i and j, $l^{ij}$are the corresponding interfaces between the phases l, a, and s, for liquid, air, and solid, respectively. Introducing $l_{\text{ext}}=2R\theta$ (the external drop surface), $l_{\text{base}}=2R\sin\theta$ (the geometric drop base surface), l_{total} (the total solid sample surface), x (the penetration depth of water in the asperities) see Figure 1. When the microscale stay in the transition wetting state and nanoscale stay in the transition wetting state, the free energy of the wetting state ($1-\cos\alpha_1<\eta_1<1$, $1-\cos\alpha_2<\eta_2<1$, $\eta_1=x_1/R_1$, $\eta_2=x_2/R_2$) is:

$$F_1=\gamma^{la}[l_{ext}+(1-f_1)l_{base}+f_1(1-f_2)l_{base}]+\gamma^{sl}f_1f_2\frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}}\frac{\arccos(1-\eta_2)}{\sqrt{\eta_2(2-\eta_2)}}l_{base}+\gamma^{sa}[(1-f_1+\frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}}f_1]r_2l_{base}($$
$$+f_1\frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}}(1-f_2+\frac{\arccos(1-\eta_2)}{\sqrt{\eta_2(2-\eta_2)}})l_{base}+r_1r_2(l_{total}-l_{base})]=\gamma^{la}l_{ext}+C_1\gamma^{la}l_{base}+\gamma^{sa}l_{total}r_1r_2$$

16)

Where

$$C_1=-\{f_1f_2\frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}}\frac{\arccos(1-\eta_2)}{\sqrt{\eta_2(2-\eta_2)}}\cos\theta_Y+f_1(f_2\text{-}1)+f_1-1\} \tag{17}$$

The normalized free energy

$$F^*=\frac{F-\gamma^{sa}l_{total}r_1r_2}{2\gamma^{la}S^{1/2}}=\frac{\theta+C(\eta_1,\eta_2)\sin\theta}{(\theta-\cos\theta\sin\theta)^{1/2}} \tag{18}$$

Define X=cosθ,

$$\frac{\partial F^*}{\partial X}=0 \tag{19}$$

We obtain

$$\cos\theta_1=f_1f_2\frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}}\frac{\arccos(1-\eta_2)}{\sqrt{\eta_2(2-\eta_2)}}\cos\theta_Y+f_1(f_2\text{-}1)+f_1-1 \tag{20}$$

When $\eta_1=1-\cos\alpha_1$, $\eta_2=1-\cos\alpha_2$, one can obtain

$$\cos\theta_{Cc}=\frac{\alpha_1}{\sin\alpha_1}\frac{\alpha_2}{\sin\alpha_2}f_1f_2\cos\theta_Y+f_1f_2-1 \tag{21}$$

The transition state will be occurring when the transition from Cc to Wc, In Eq (6), we set $\eta_2=1-\cos\alpha_2$, one can obtain

$$\cos\theta_{\text{Cc-Wc}} = f_1 f_2 \frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}} \frac{\alpha_2}{\sin\alpha_2} \cos\theta_Y + f_1 f_2 - 1 \tag{22}$$

Substitute Eq (8) into Eq (4), one can obtain the free energy barrier $F^*_{Cc\text{-}Wc}$

The transition state will be occurring when the transition from Cc to Cw, in Eq (6), we set η_1=1-cosα_1, one can obtain

$$\cos\theta_{\text{Cc-Cw}} = f_1 f_2 \frac{\alpha_1}{\sin\alpha_1} \frac{\arccos(1-\eta_2)}{\sqrt{\eta_2(2-\eta_2)}} \cos\theta_Y + f_1 f_2 - 1 \tag{23}$$

Substitute Eq (9) into Eq (4), one can obtain the free energy barrier $F^*_{Cc\text{-}Cw}$

When the micro scale stay in the transition wetting state and nanoscale stay in the Wenzel wetting state, the surface energy of the state (1-cosα_1<η_1<1, η_2=1, η_1=x_1/R$_1$, η_2=x_2/R$_2$) is:

$$\begin{aligned} F_1 &= \gamma^{la}[l_{ext} + (1-f_1)l_{base}] + \gamma^{sl} r_2 f_1 \frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}} l_{base} + \gamma^{sa}[r_1 r_2 (l_{total} - l_{base}) + r_2(1-f_1)l_{base} + r_2 f_1 \frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}} l_{base}] \\ &= \gamma^{la} l_{ext} + C_2 \gamma^{la} l_{base} + \gamma^{sa} l_{total} r_1 r_2 \end{aligned} \tag{24}$$

Where

$$C_2 = -[r_2 f_1 \frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}} \cos\theta_Y + f_1 - 1] \tag{25}$$

The transition state will be occured when the transition from Cw to Ww, one can obtain

$$\cos\theta_{Cw-Ww} = r_2 f_1 \frac{\arccos(1-\eta_1)}{\sqrt{\eta_1(2-\eta_1)}} \cos\theta_Y + f_1 - 1 \tag{26}$$

Substitute Eq (26) into Eq (18), one can obtain the free energy barrier $F^*_{Cc\text{-}Cw}$

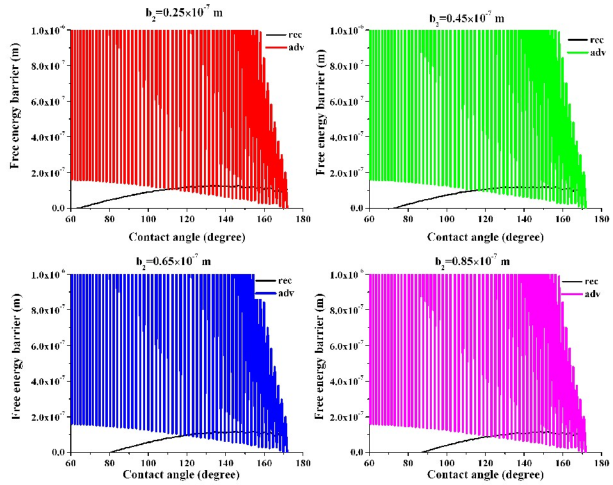

Fig. S2 Dependent of normalized advancing and receding FEBs against apparent CA for Cc wetting states with different Nano base space b_2 ($L = 10^{-2}$ m, $R_1 = b_1 = 1\times10^{-5}$ m, $R_2 = 1\times10^{-7}$ m, intrinsic CA, $\theta_Y = 120^o$).

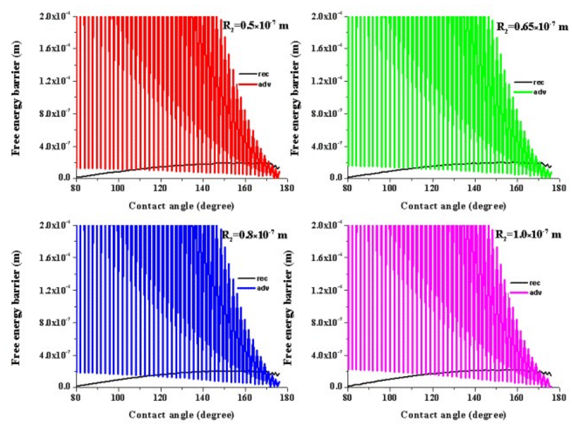

Fig. S3 The advancing and receding FEBs of Cw wetting states for dual semicircular structure with different nano-radius R_2 ($L = 10^{-2}$ m, $R_1 = b_1 = 1\times10^{-5}$ m, $b_2 = 1\times10^{-7}$ m, intrinsic CA, $\theta_Y = 120^o$).

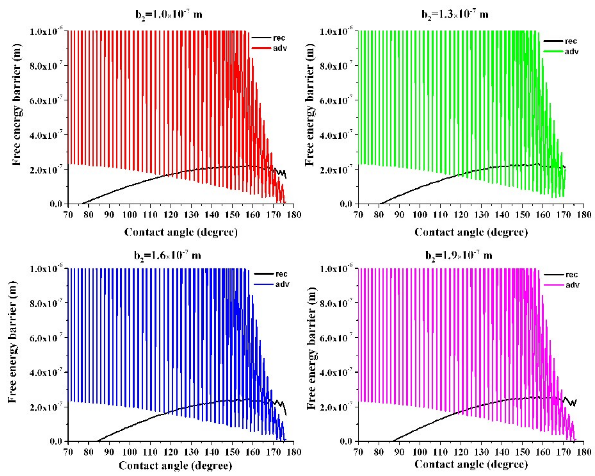

Fig. S4 The advancing and receding FEBs of Cw wetting states for dual semicircular structure with different nano- radius b_2 (L = 10^{-2} m, R_1 = b_1 = 1×10^{-5} m, R_2 = 1×10^{-7} m, intrinsic CA, θ_Y = 120^o).

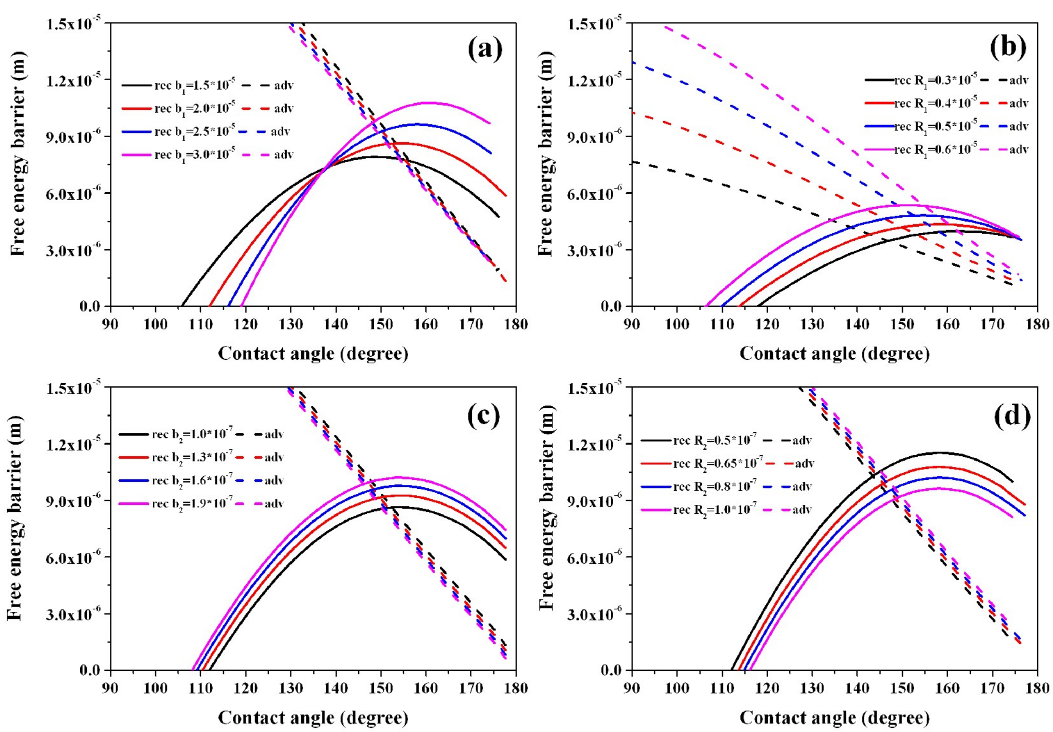

Fig. S5 (a) The advancing and receding FEBs of Ww wetting states for dual semicircular structure with different (a) micro-semicircular base space b_1 (L = 10^{-2} m, R_1 = 1×10^{-5} m, R_2 =1×10^{-7} m ,b_2 = 1×10^{-7} m, intrinsic CA, θ_Y = 120^o); (b) micro-semicircular base radius R_1 ($L = 10^{-2}$ m, $b_1 = 1\times10^{-5}$ m, $R_2 = 1\times10^{-7}$ m ,$b_2 = 1\times10^{-7}$ m, intrinsic CA, $\theta_Y = 120^o$); (c) Nano-semicircular base space b_2 ($L = 10^{-2}$ m, $b_1 = 2\times10^{-5}$ m, $R_2 = 1\times10^{-7}$ m ,$R_2 = 1\times10^{-5}$ m, intrinsic CA, $\theta_Y = 120^o$); (d) Nano-semicircular base radius R_2 ($L = 10^{-2}$ m, $R_1 = 1\times10^{-5}$ m, $b_1= 2\times10^{-5}$ m ,$b_2 = 1\times10^{-7}$ m, intrinsic CA, $\theta_Y = 120^o$)

3. Experiment

3.1 Materials.

Woods were provided from a local supermarket. TiO2 was supplied by Sigma-Aldrich and used as received. Foraperle 323 was purchased by DuPont. All other chemicals were analytical-grade reagents.

3.2 Fabrication of waterborne distinctive superlyphobic coatings

The stable TiO_2 nanoparticles water solution was prepared according to the ratio of quality with TiO_2, Foraperle 323 (F323) and water is 1:1:10. The woods were cleaned with acetone, ethanol and water. The clean fabrics were immersed in the stored TiO_2 nanoparticle water solution for about 5 min at room temperature. Then, the fabrics adsorbed with TiO_2 nanoparticle and F323 were heated to 130 ^{o} C for an hour.

3.3 Instrumentation and characterization.

The water contact angles and slide angles were measured by POWEREACH JC2000D goniometer (China). SEM images detected from JEOL JSM-5600LV scanning electron microscopes with Au-sputtered specimens. The surface composition of the samples was investigated by XPS (X-ray photoelectron spectroscopy, Physical Electronics, USA VG ESCALAB 250).

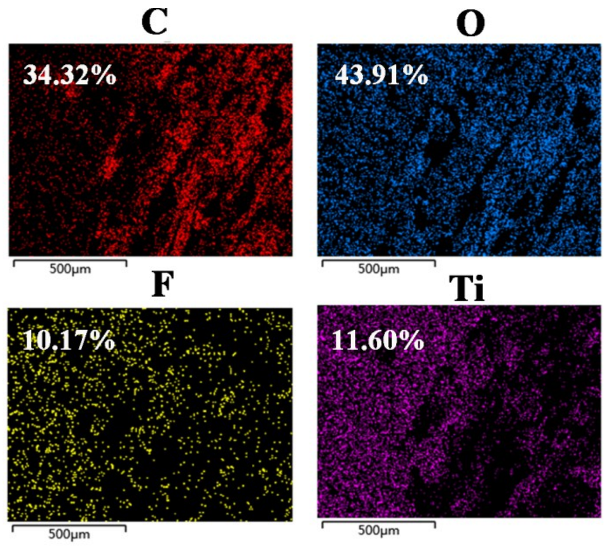

Fig. S6 EDS image of TiO_2 - F323 coating on wood.

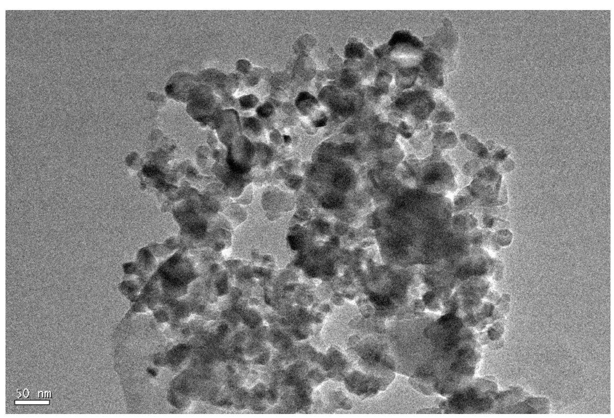

Fig. S7 TEM image of TiO_2 nanoparticles.