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Supplementary Materials: Mechanical Equilibrium Dynamics Controlling Wetting State Transition at Low-Temperature Superhydrophobic Array-Microstructure Surfaces

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1. Surface Fabrication

Preparation of hydrophobic SiO_2 nanoparticles. The 0.3 mL 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (PFDTES) was first mixed with ethanol (40 mL) and the solution system was stirred for 60 min at room temperature. Next, 1.5 g of SiO_2 nanoparticles was added into the 10 mL ammonium hydroxide solution to form SiO_2 suspension, and the SiO_2 suspension was dispersed by ultrasonic for 15 min. Afterward, the SiO_2 suspension was slowly transferred into the above-prepared PFDTES solution followed by continuous magnetic stirring for 24 h at 40 °C. The obtained precipitate was further centrifuged at 10,000 rpm for 5 min, and then washed twice with ethanol. Finally, the products were vacuum dried to obtain the hydrophobic SiO_2 nanoparticles, which were labeled as F-SiO_2.

2. Surface Characterization

Characterizations of superhydrophobic surfaces. The three-dimensional topographies were captured by a 3D microscope with super wide depth of field (DVM6, Wetzlar, Germany). The micro morphologies of the sample were observed using a field emission scanning electron microscopy (FE-SEM; Hitachi S4800, Tokyo, Japan). The chemical compositions of F-SiO_2 nanoparticles were directly detected by an X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Fisher Scientific Inc., Waltham, MA, USA). The contact angle of a 10 μL water droplet on the superhydrophobic surface was measured by a contact angle analyzer (Kruss DSA100, Hamburg, Germany). The average value of three measurements was determined.

Chemical composition of F-SiO_2 nanoparticles. XPS spectra were obtained to further confirm the surface chemical compositions of large micron cylinder and cylinder sprayed by F-SiO_2 nanoparticles. As shown in Figure S(1a), the pillar array structure was sprayed by F-SiO_2 nanoparticles increases the intensity of Si 2p, C 1s, O 1s, and F 1s peaks. It is clear that there are four components in the C 1s high-resolution spectrum (see Figure S2b), which are located at 280.0 eV (C–Si), 284.7 eV (C–C/C–H), 288.2 eV (C-O-C), and 292.7 eV (C–F). The bonds of C–Si, C–C/C–H, and C–F are ascribed to PFDTES molecules, and C-O-C is attributed to the photoresist. Notably, it can be seen that the F element only exists on the surface of the F-SiO_2 nanoparticles (see Figure S(1c)). This prominent peak is associated with the CF_2 (at 684.9 eV) and CF_3 (at 689.4 eV) groups of PFDTES molecules, which have low surface energy and endow the F-SiO_2 nanoparticles with excellent hydrophobi-

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city. Also, the Si 2p high-resolution spectrum can be resolved into two components assigned to Si–C (at 100.9 eV) and Si–O–Si (at 103.4 eV). All of this Si–C component originates from PFDTES, whereas Si–O–Si is the newly formed chemical covalent bonds between PFDTES and SiO_2 nanoparticles.

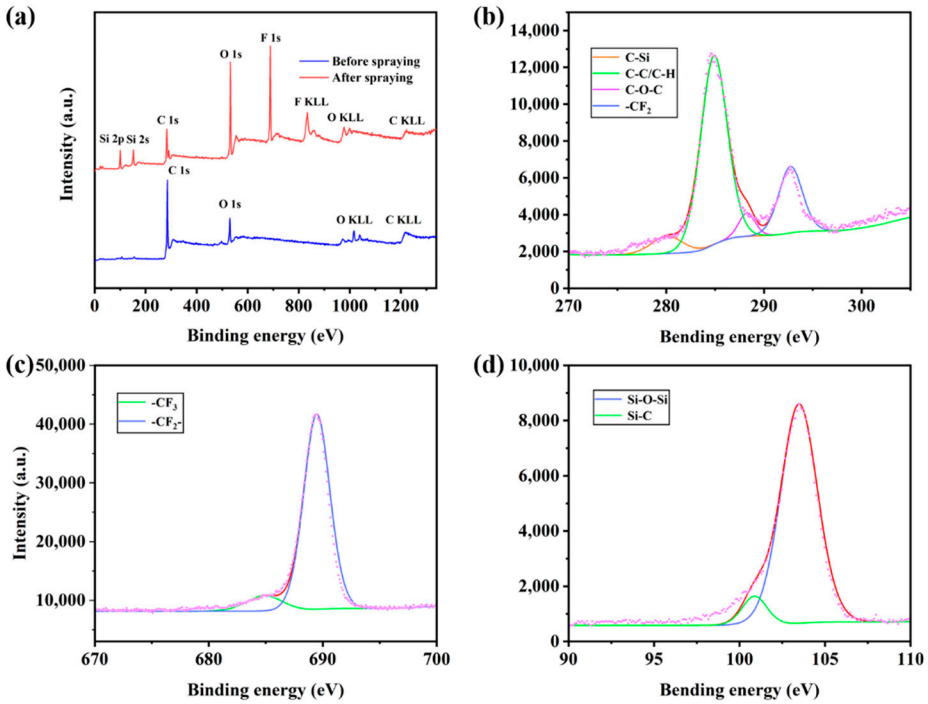

Figure S1. (**a**) XPS survey spectra of substrate before and after spraying. (**b**) High-revolution spectra of sprayed substrate for C 1s. (**c**) High-revolution spectra of sprayed substrate for F 1s. (**d**) High-revolution spectra of sprayed substrate for Si 2p.

3. Experimental Setup and Testing Process

Experimental setup. Experiments are conducted on a controlled temperature refrigeration station, as shown in Figure S2. The experimental setup consists of a refrigeration system, a temperature measuring system, and a visualization system. The surface temperature, ambient temperature, and relative humidity are carefully controlled throughout the experiment.

Low-temperature wetting behavior tests. The superhydrophobic sample was placed on a refrigeration platform, and a 10 μL droplet can nearly suspend on the surface. Subsequently, the temperature of sample surfaces was controlled by refrigeration system from room temperature to zero degree Celsius, and the wetting behavior was recorded by a CCD camera. In order to obtain the accurate surface temperature, temperature measuring system was used to record the real-time surface temperature, which recorded a temperature value for every second. Figure S3 illustrates the temperature curve and the relationship between surface temperature and time under cooling conditions.

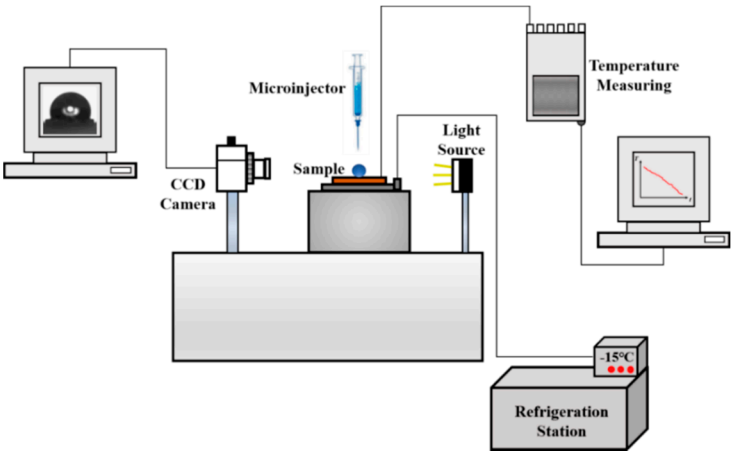

Figure S2. Schematic diagram of the experiment setup.

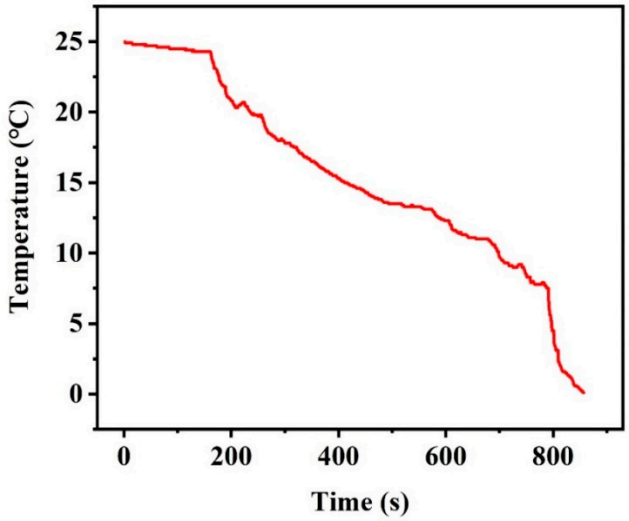

Figure S3. The real-time surface temperature under cooling conditions.

4. Analysis of Work Done Against Resistance

According to the analysis of work done against resistance, the penetration depth on the H2 and H3 surfaces reflects the relationship of work done against resistance. The penetration results the decrease of the droplet volume on the superhydrophobic surface, the penetration depth can be easily obtained by change of droplet volume. We assume that penetration is an ideal state, the area of liquid-air interface is constant, which is expressed as S. The volume of a droplet on the superhydrophobic surface is $V = \frac{1}{3}\pi R^3(1-\cos\theta)^2(2+\cos\theta)$, R is the radius of a 10 μL droplet. Therefore, the penetration depth is $\Delta H = \frac{\pi R^3(1-\cos\theta_1)^2(2+\cos\theta_1) - \pi R^3(1-\cos\theta_2)^2(2+\cos\theta_2)}{3S}$, θ_1 and θ_2 are the contact angle (CA) for the initial Cassie-Baxter wetting state and C-W wetting transition point. Here, the θ_1 on H2 and H3 surfaces are 150.4° and 150.7°, and the θ_2 are 144.5° and 140.3°, respectively. According to the CA, the penetration depth on the H2 and H3 surfaces can be obtained, which are expressed as ΔH_2 and ΔH_3 respectively. The relationship of the penetration depth on the H2 and H3 surfaces is $\Delta H_3 \approx 2\Delta H_2$. The

work done against resistance on the H2 and H3 surfaces are expressed as W_{H2} and W_{H3}, the relationship is $\frac{W_{H2}}{W_{H3}} = \frac{\Delta H_2}{\Delta H_3}$.

5. Supplementary Videos

Video S1. A 10 μL droplet on the superhydrophobic surface with the pillar height of 200 μm continuously changes at 0–25 °C.

Video S2. A 10 μL droplet on the superhydrophobic surface with the pillar height of 250 μm occurs the wetting state transition from a Cassie-Baxter state to a Wenzel state.

Video S3. A 10 μL droplet on the superhydrophobic surface with the pillar height of 300 μm occurs the wetting state transition from a Cassie-Baxter state to a Wenzel state.