Supporting Information

Antifouling performance against SiO_2 particulate matter adhesion of Cyclo Olefin Polymer nanopillar surfaces

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1. Preparation of Anodic Aluminum Oxide (AAO) Mold

1.1 Electropolishing

Regularly arranged nanoholes were prepared using anodic aluminum oxide (AAO), which have high verticality. Here, the surface of the substrate must be flat. However, due to aluminum (Al) plate mechanical polishing and storage methods, its surface has microdamage, oxide, and other irregularities on the plate surface. Since these are thought to harm the regular arrangement of nanoholes, an electropolishing process was performed to remove the irregularities on the surface. The conditions for electropolishing are shown in the Table S1 and written in below. An Al plate was connected to the anode side and a platinum (Pt) plate to the cathode side in a mixed solution of perchloric acid and ethanol (50 mL: 200 mL), and a voltage of 10 V was applied for 15 min with a DC power (E3616 DC POWER SUPPLY, Hewlett-Packard Company). A cooling system (water pool type) was used to keep the solution temperature below 10 °C during polishing. After polishing, the Al plates were immersed in pure water and cleaned with ultrasonic measures for 5 min.

Table S1. Electropolishing Conditions

Electrolytic polishing liquids	Perchloric acid（$HClO_4$）: 50 mL Ethanol（C_2H_6O）: 200 mL
Processing time [min]	15
Applied voltage [V]	10
Temperature [°C]	0

1.2 The First Anodizing

In this study, we introduced two-step anodization to obtain regularly arranged nanoholes for the mold. The first anodization is carried out after the electropolishing and important to decide the pitch of nanoholes. Patterns of 200 nm in pitch were produced to mimic the nanotopolography of the cicada wing.

The Al plate was connected to the anode of a DC power supply (2400, Keithley Instruments, Inc.), and the platinum (Pt) wire to the cathode. To obtain the pitch of 200 nm, 85 V voltage was applied for more than 15 min with oxalic acid (0.3 M) as the electrolyte kept at 0 °C by a cooling system to perform the first anodic oxidation as

shown in Table S2. By contrast, for the 100 nm pitch pattern obtained, the voltage was decreased to 40 V, but it was kept for 20 hours in oxalic acid action (0.3 M) at 0 °C. In addition to 300 nm-pitch fabrication, Hard Anodization[2] was performed using 0.3 M oxalic acid as the electrolyte, and 140 V as the applied voltage. The initial voltage was 40 V and anodic oxidation was performed for 8 min. Thereafter, the voltage was increased to 140 V with linearly increasing voltage of 0.0125 V/s, and finally all steps were performed for a total of 1.5 hours.

Table S2. The 1st anodizing conditions from100 nm to 300 nm in pitches.

Pitch [nm]	200
Electrolyte	Oxalic Acid ($H_2C_2O_4$, 0.3 M)
Applied voltage [V]	40
Time [min]	> 15
Temperature [℃]	0

1.3 Anodic Aluminum Oxide (AAO) Etching

The substrate was immersed in the selective etching solution to etch the AAO layer obtained in the first anodization selectively. The mixture etching solution containing phosphoric acid (H_3PO_4, 6 wt %) and chromium trioxide (CrO_3, 1.8 wt %), was kept constant at the temperature shown in Table S3. After sufficient first anodization, regularly arranged indentation according to nanopore formation appeared on the surface of the etched Al plate.

Table S3. Anodic aluminum oxide etching conditions for three kinds of pitches.

Pitch [nm]	200
Etching solutions	Phosphoric Acid (H_3PO_4, 6 wt %) Chromium Trioxide (CrO_3, 1.8 wt %)
Time [min]	20
Temperature [℃]	60

1.4 The Second Anodizing

The second anodization of Al was done as same as the first anodization. To elucidate the effect of the dimensions of the structures on the bactericidal properties, the heights

of the nanostructures were adjusted for each of the three types of pitch patterns. The structure parameters and anodization conditions are shown in the Table S4.

Table S4. The second anodizing conditions for three nanopillar AAO templates.

Pitch [nm]	200
Depth [nm]	100
Electrolytic Solution	Oxalic Acid ($H_2C_2O_4$, 0.3 M)
Applied voltage [V]	85
Time [min]	0.5
Temperature [°C]	0

1.5 Widening

Widening process was performed to enlarge the pore size of the nanoholes. Al plates were immersed in a phosphoric acid (5 wt %) solution at 34 °C. In this study, the three target diameters (Table S5) were fabricated at the nanohole diameter with widening speed of 2.6 nm/min.

Table S5. Widening conditions of three kinds of nanopillar AAO templates.

Pitch [nm]	200
Diameter [nm]	100
Solution	Phosphoric acid (H_3PO_4, 5 wt %)
Time [min]	25
Temperature [°C]	34

1.6 Mold Release Reagent Application

The mold spat (W-6847-AL, AGC Seimi Chemical Co., Ltd., Kanagawa, Japan) was used as a mold release reagent to improve the mold release performance of AAO molds. The AAO molds were ultrasonically cleaned in acetone, ethanol, and water for 5 minutes, respectively, and then dipped into in a release agent for 5 minutes. After the substrate was cleaned using DI water, the moisture on the surface of the AAO mold was dried in a heating process.

2. Fabrication of nanopillar structures by Thermal Nanoimprint lithography (T-NIL)

COP film (50 mm x 50 mm x1 mm, glass transition temperature: 163 °C), one of thermoplastic resins, was used as a substrate. The T-NIL system (G-12RS2000, Orihara Industrial Co. Ltd.) allows the programming of heating temperature, applied pressure, and processing time.

2.1 Preheating

When performing T-NIL, no plastic deformation occurs unless the resin to be molded is above its glass transition temperature of 163 °C. Therefore, preheat the up and down heater before applying pressure. The preheating temperature was set to 180 °C, and preheated for 5 minutes. When the entire system fully reached the set temperature, the preheating was considered complete.

2.2 Heating and pressurizing

The pressure and pressurization time were set at 4.2 MPa, 10 minutes for all samples.

2.3 Cooling

Maintain the pressure and ~~only~~ reduce the temperature gradually until it is lower than the glass transition temperature. Here, this temperature was set as 150 °C. After the stage temperature reached to 150 °C, the pressure was set to release automatically.

2.4 Demolding

Remove the system from the platform and peel off the resin and AAO. Since the adhesion between the resin film and AAO is weak due to the mold release reagent, so we use tweezers to release the mold.

3. Self-cleaning Tests

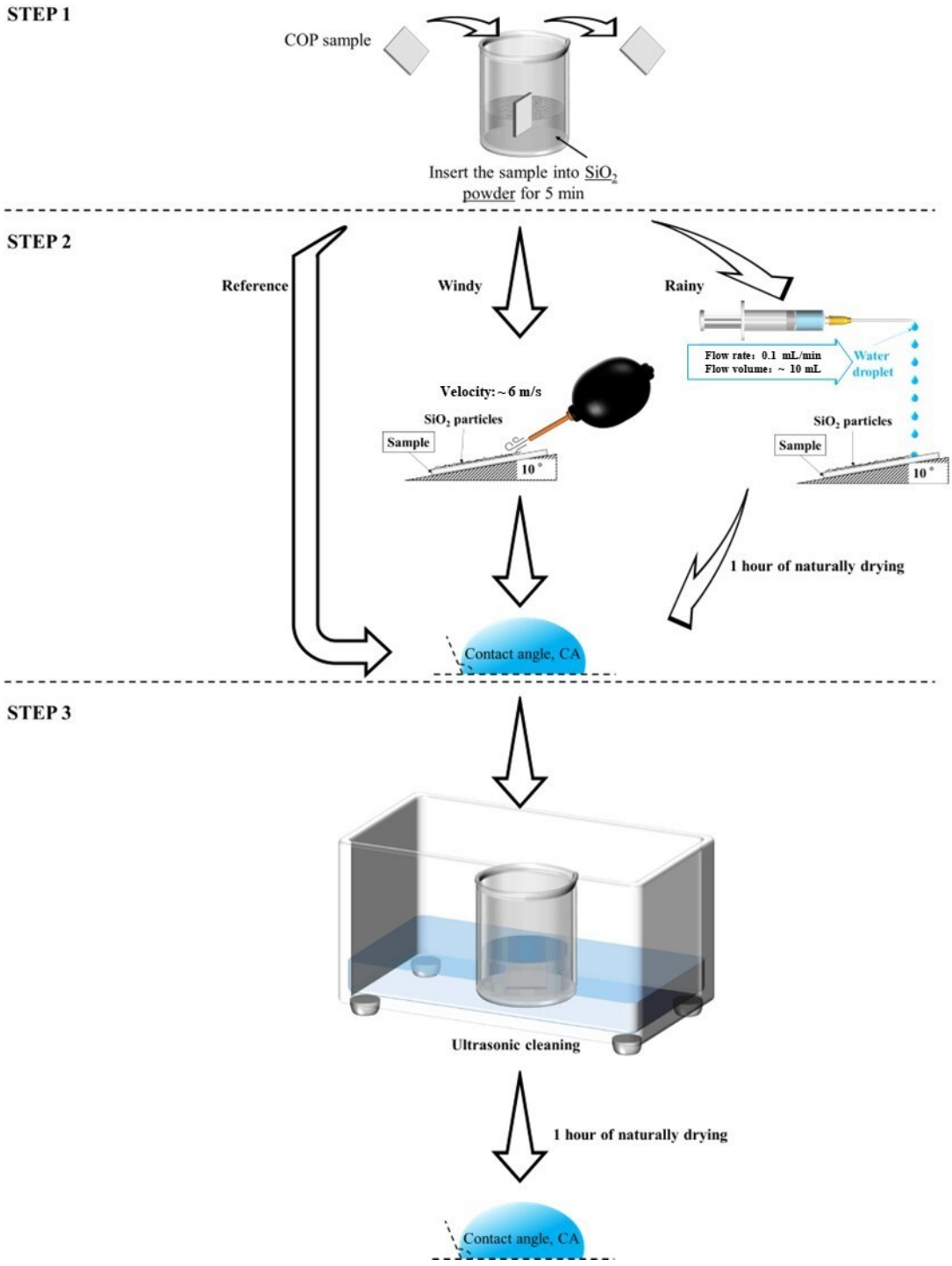

Fig. S1 The methods of self-cleaning tests.

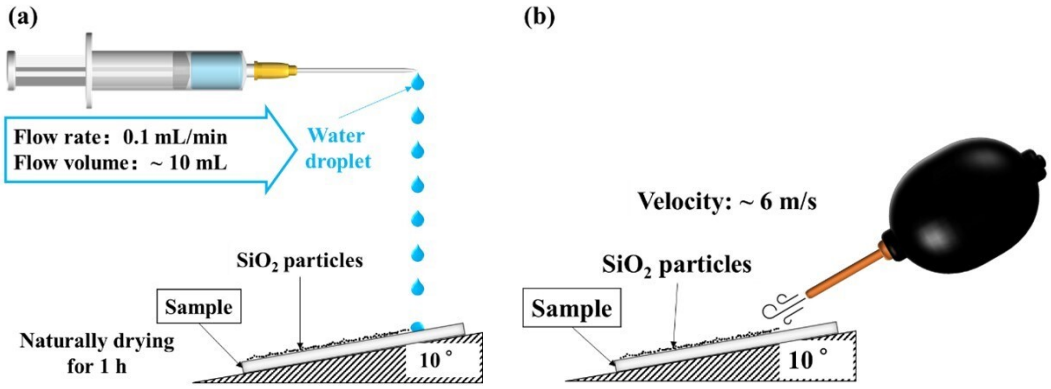

Fig. S2 Cleaning methods for substrate surfaces. (a) natural raindrops, and (b) wind conditions use droplets from a syringe and wind from an air blower, respectively.

Table S6. WCAs of sample in the self-cleaning test processes. BUC and AUC stand for before (Fig. S1, Step2) and after (Fig. S1, Step3) the ultrasonic cleaning, respectively.

Sample	Original	Reference		Windy		Rainy	
		BUC	AUC	BUC	AUC	BUC	AUC
Reference	96.4 ± 1.0	99.8 ± 2.4	97.1 ± 7.0	99.1 ± 0.7	99.0 ± 1.0	91.5 ± 2.5	96.4 ± 2.8
H200	146.6 ± 1.3	148.6 ± 2.0	140.6 ± 2.1	144.3 ± 1.7	143.4 ± 3.6	129.8 ± 1.4	130.2 ± 3.7
H250	152.8 ± 1.6	143.0 ± 4.2	146.8 ± 5.2	148.0 ± 3.4	147.3 ± 1.5	142.5 ± 3.3	146.1 ± 2.3
H300	148.8 ± 6.1	143.9 ± 7.5	146.6 ± 8.6	143.8 ± 7.0	144.5 ± 4.6	137.0 ± 5.3	140.6 ± 2.6
H350	154.0 ± 3.8	139.7 ± 5.7	145.7 ± 4.9	148.3 ± 4.3	142.5 ± 5.2	149.6 ± 4.7	150.1 ± 1.1

The flow chart of the three self-cleaning tests in this study is shown in Fig. S1. First, to fully contact the COP sample with the SiO_2 dust, the COP sample was inserted into the dry SiO_2 dust for 5 minutes. The sample was taken out and placed on a 10° platform we made using 3D printing technology. After that, we set up two experimental methods to simulate the outdoor environment of wind and rain, and a reference group. For the wind environment, we use an air blower to clean the samples that have just been removed from the SiO_2 dust, and measure the WCA on the sample surface (Fig. S2 a). In contrast, we used droplets falling from a syringe to simulate rainy conditions (Fig.

S2 b). The WCA of the sample surface was measured after being washed with water droplets within 10 mL and allowed to dry naturally for 1 hour. We directly measured the WCA on the sample surface for the reference group. Finally, we used the ultrasonic cleaning method to clean the samples to clean the solid particles further weakly attached to the sample surface. We measured the WCA on the sample surface after natural drying for one hour. (Details in Table S7)

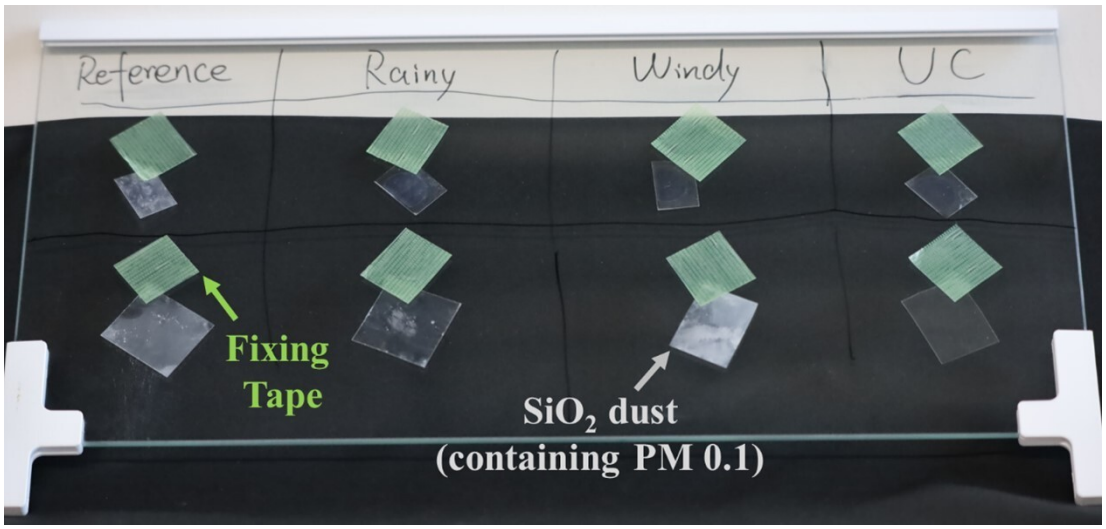

Fig. S3 Photos of cleaning results of SiO_2 particles applied on H250 (up) and flat (bottom) COP surfaces. UC stands for ultrasonic cleaning process. The green tape was used to fix COP samples on the glass board.

Table S7. Dynamic analysis of surface wettability. Advancing contact angle (θ_{adv}); Receding contact angle (θ_{rec}); Contact angle hysteresis (CAH); Contact radius r_c.

Sample	θ_{adv} (º)	θ_{rec} (º)	CAH (º)	r_c (μm)
Reference	102.3 ± 6.3	83.1 ± 9.7	19.2	1931.6 ± 22.1
H200	157.4 ± 1.6	136.3 ± 1.9	21.1	1068.9 ± 11.6
H250	159.0 ± 2.8	136.8 ± 2.6	22.2	1053.3 ± 22.6
H300	158.6 ± 2.1	136.5 ± 1.4	22.1	1041.6 ± 8.3
H350	160.7 ± 2.7	138.7 ± 2.1	22.0	999.6 ± 39.5

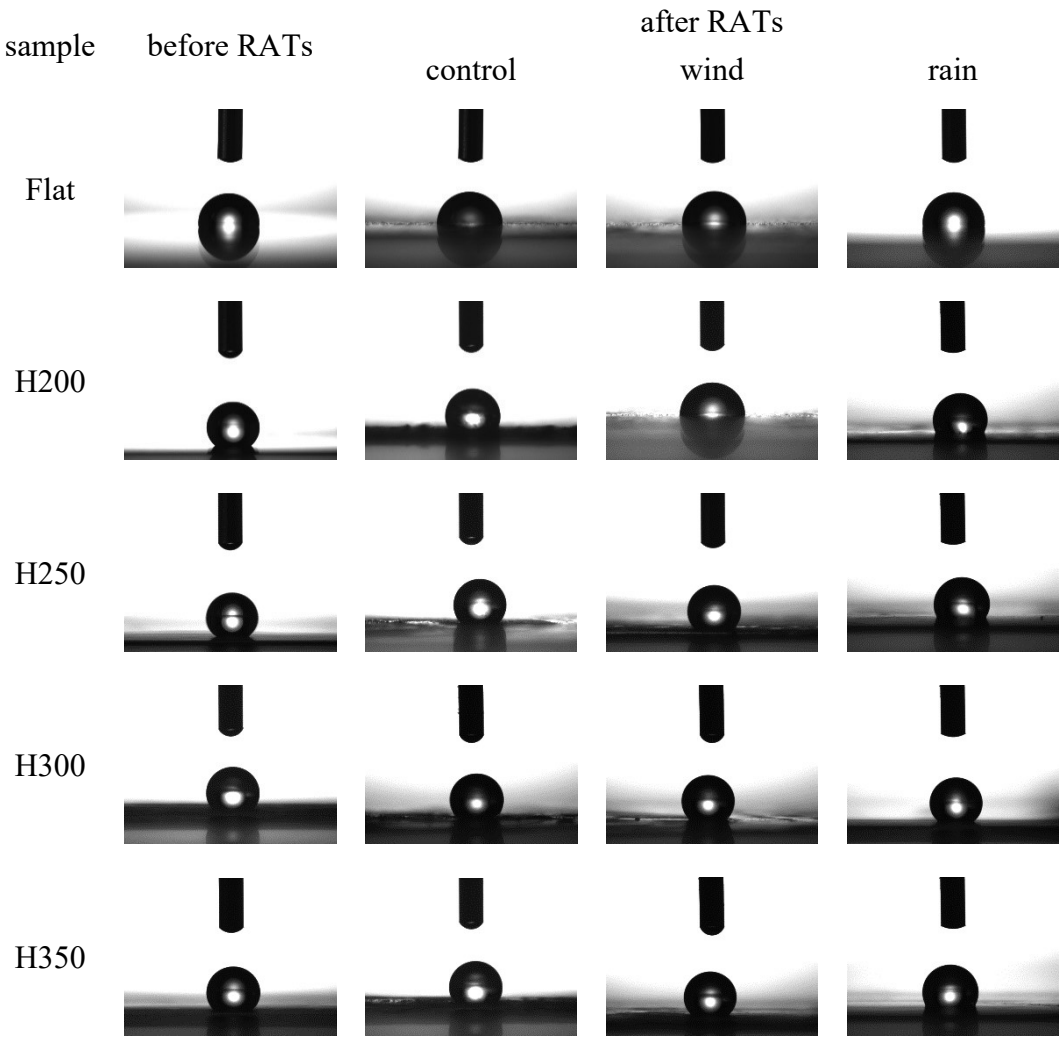

Fig. S4 Water contact angles of the sample surface before and after repeated antifouling tests (RATs, results of cycle 10). The three experimental conditions are control group (no cleaning process), wind and rain.

References

1. Lee W, Ji R, Gösele U, Nielsch K. Fast fabrication of long-range ordered porous alumina membranes by hard anodization. *Nature Materials*. 2006;5(9): 741-747. doi:10.1038/nmat1717
2. Li J, Li C, Chen C, Hao Q, Wang Z, Zhu J, et al. Facile Method for Modulating the Profiles and Periods of Self-Ordered Three-Dimensional Alumina Taper-Nanopores. *ACS Applied Materials & Interfaces*. 2012;4(10): 5678-5683. doi:10.1021/am301603e