Supporting Information

A Transparent and Photo-Patternable Superhydrophobic Film

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Experimental section.

Materials and instrumentation. TiO_2 slurry (17 w% in 2-propanol) was obtained from Tayca. Heptadecafluorodecyltrimethoxysilane (TSL 8233) was obtained from Toshiba Silicone. Sodium alginate, calcium chloride, palladium chloride and anhydrous ethanol were obtained from Wako. Chemicals for electroless plating of nickel (NM_DEN LPX) were gifts of Uemura Kogyo. All the chemicals were used as received, without further purification. Ultrapure water (Mill-Q) was used in all experiments.

Surface and cross-sectional morphologies of TiO_2 films were examined with a Hitachi S-4500 scanning electron microscope (SEM). All of the samples were coated with platinum with a commercial sputtering apparatus prior to the SEM examination. The surface roughness of the TiO_2 films was measured with a scanning probe microscope (SPM, Nanoscope IV, Digital Instruments). Particle size of TiO_2 slurry was analyzed with a transmission electron microscope (Topcon EM-002B) and a dynamic light scattering particle size analyzer (Horiba, LB-500). Contact angles (CA), either static or dynamic, were measured with a contact angle meter (Kyowa CA-X) at room temperature and were analyzed with commercial FAMAS software. Optical microscopes, such as a Keyence VH-Z100 and a Keyence VF-7500 were used to study the superhydrophobic-superhydrophilic pattern. A cooling/heating stage (Japan Hightech Co., Code 10021) was used to cool or heat sample during observation with optical microscopes.

Preparation of superhydrophobic TiO_2 films. TiO_2 slurry (Tayca, TKD 701) was diluted with anhydrous ethanol (Wako) to a concentration of 2% by weight. TiO_2 films were prepared by spin-coating the slurry on glass substrates for 5 times. The film was heated at 120 °C for 5 minute after each coating, and was heated at 500 °C for 30 minute finally. The resultant TiO_2 film has a thickness of 500 nm.

The TiO_2 film was modified with heptadecafluorodecyltrimethoxysilane (Toshiba silicone, TSL 8233) by the chemical vapor deposition (CVD) method. In brief, TiO_2 film was put in a vessel filled with dry N_2. A drop (0.2 ml) of the fluoroalkylsilane (FAS) was pipetted into the vessel. After that, the vessel was heated at 120 °C for 3 hours. Finally, the modified TiO_2 film was rinsed with ethanol to remove physisorbed FAS molecules.

We have also prepared TiO_2 films with different thickness via spin-coating the TiO_2 slurry for 1, 3, 7, and 10 times, respectively in order to examine the influence of film thickness on the transparency of TiO_2 films. As shown in Figure S3, the light transmittance of TiO_2 films decreases with the increase of coating times due to the enhanced light scattering. But even for a 10-time coated film whose thickness is 1 μm, its transmittance is over 68% in the visible light region (400-800 nm) and thus is transparent.

Patterning superhydrophobic film. Parallel UV irradiation (Yamashita Denso, Hypercure 200) was used to pattern the FAS-modified TiO_2 film through a photomask made by depositing a 100 nm-thick chromium pattern on a 2 mm-thick quartz plate. The intensity of UV irradiation was measured as 27 mW cm^{-2} with a Hamamatsu photometer. The superhydrophobic-superhydrophilic pattern was visible by optical microscopes when cooled below the dew point with a cooling/heating stage.

Electroless deposition of nickel. The patterned TiO_2 film was immersed in 10 mM $PdCl_2$ in mixture of water and ethylene glycol (100: 2 by volume), and then was illuminated with weak UV light (1 mW cm^{-2}) for 10 second. After these procedures, the patterned surface was immersed in an electroless plating bath of nickel (NM_DEN LPX) at 90 °C for 30 min.

Alginate hydrogel pattern. The patterned TiO_2 film was immersed in a 2% w/w sodium alginate solution in water and withdrawn at a speed of 15 cm min^{-1}. By this procedure, the superhydrophilic area of the patterned surface was filled with alginate solution. Next, the film was immersed in a 2% calcium chloride aqueous solution for 20 second and then withdrawn from the solution. Calcium ions could crosslink alginate chains and cause the formation of alginate hydrogel pattern on TiO_2 film.

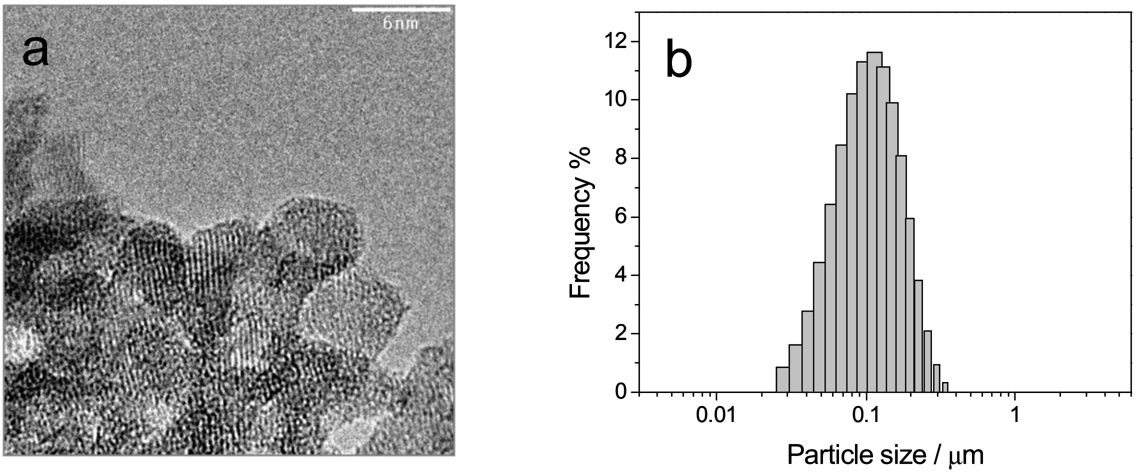

Figure S1. a) TEM image of TiO_2 nanoparticles and b) DLS size distribution of TiO_2 aggregated particles in the slurry used in preparation of TiO_2 film.

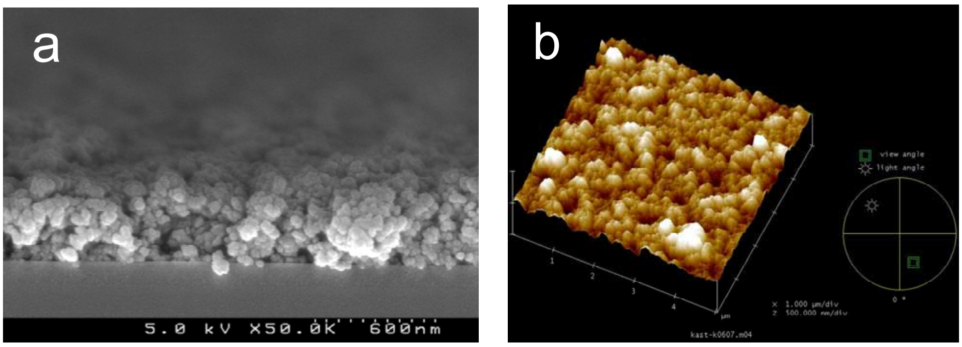

Figure S2. a) Cross-sectional SEM image of TiO2 film and b) surface topography picture measured by a SPM.

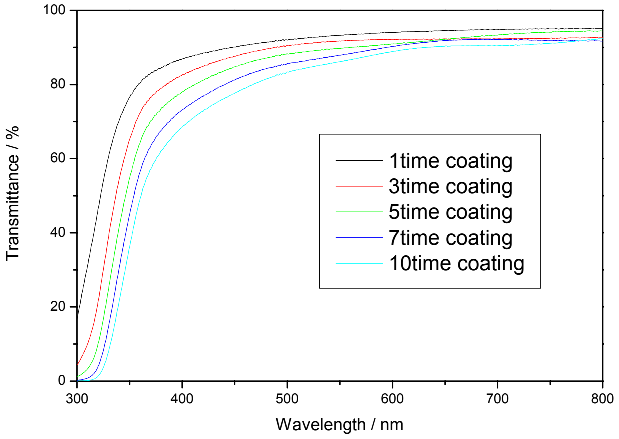

Figure S3. Transmission spectra of TiO_2 films prepared by spin-coating a TiO_2 slurry for 1, 3, 5, 7, and 10 times, respectively.

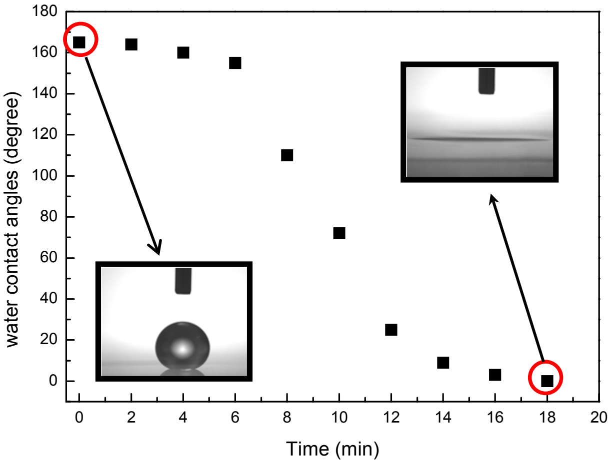

Figure S4. Evolution of water contact angle on a superhydrophobic TiO_2 film as a function of UV illumination time. Also shown in the figure are two pictures corresponding to the superhydrophobic and superhydrophilic states, respectively.

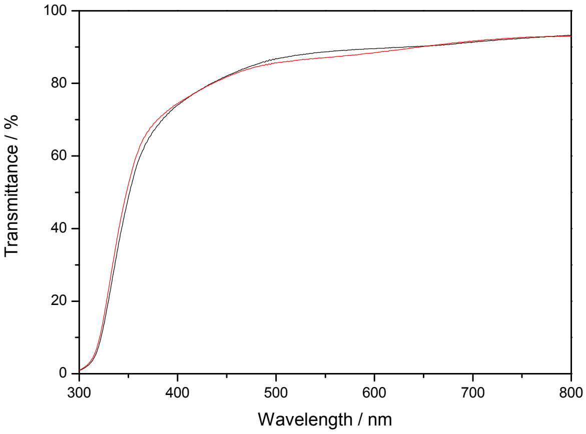

Figure S5. Transmission spectra of a superhydrophobic TiO_2 film (black line) and the film patterned with UV irradiation through a photomask (red line). Photocatalytic decomposition of fluoroalkylsilane monolayer with UV light did not change the transparency of the film appreciably.

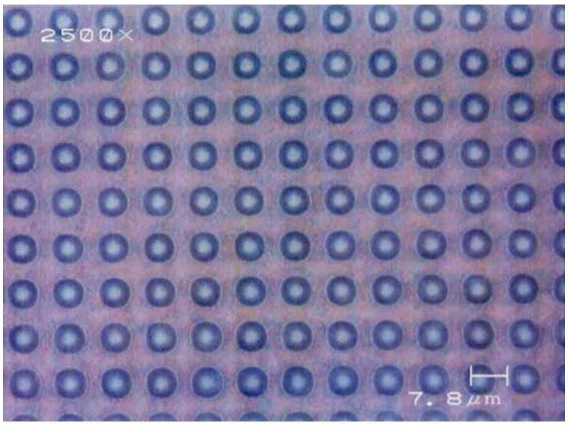

Figure S6. Micrograph of a superhydrophobic TiO_2 film patterned with UV light through a photomask that consists of 5 μm-wide squares. The micrograph was taken when cooling the film below the dew point so that water was site-selectively condensed in the superhydrophilic area.

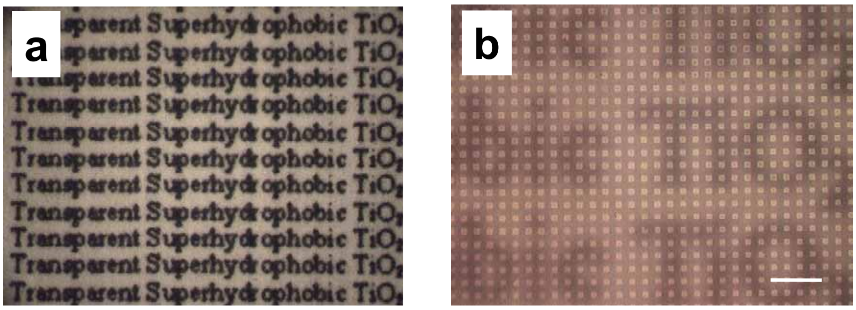

Figure S7. a) Picture of an alginate hydrogel pattern on a superhydrophobic TiO_2 film showing the transparency of the patterned film. b) Optical micrograph of the alginate hydrogel pattern taken at 100-time-magnification. The characters under the hydrogel pattern are a bit vague because they are out of focus. The bar in Figure S6b corresponds to 400 μm.

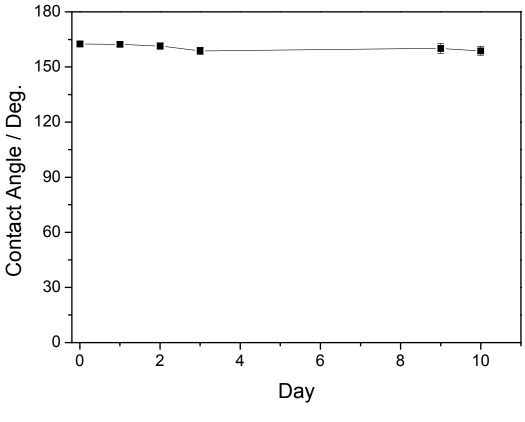

Figure S8. Temporal evolution of water contact angle of a superhydrophobic TiO_2 film placed under fluorescent lamps. The film shows stable superhydrophobic property (water contact angle > 160°) for over 10 days. The emission of fluorescent lamps contains visible light and a small amount of ultraviolet light (UV intensity: 1.2 μW cm^{-2}).