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Electronic Supplementary Information (ESI)

"Non-sticky" superhydrophobic surface by self-assembly of fluoroalkyl phosphonic acid on a hierarchically micro/nanostructured alumina gel film

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Materials. Aluminum tri-sec-butoxide (Al(O-sec-Bu)$_3$) (99.99%) and Ethyl acetoacetate were purchased from Sigma Aldrich and Tokyo Chemical Industry, respectively. Isopropyl alcohol and alumina nanoparticle were purchased from WAKO Pure Chemical Industries. 1*H*,1*H*,2*H*,2*H*-perfluorodecyl phosphonic acid (FDPA) was purchased from DOJINDO Laboratories. They were all used as received.

Instrumentation. Scanning electron microscopy (SEM) was acquired using a Hitachi S-4300SE field emission scanning electron microscope at an accelerating voltage of 5 kV. The static contact angles were measured on an Attension Theta system (KSV Instruments Ltd.). A water drop (5.0 μL) was lowered onto the sample surface from a needle tip. The videos of water drops departing and sliding on surfaces were taken on a drop-shaped analytical system DSA 10 Mk2 (A. KRÜSS Optronic GmbH, Hamburg, Germany) equipped with a tilting stage and a video camera. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an XPS-APEX (Physical Electronics Inc., Chanhassen, MN) using a monochromatic Al-K_α X-ray source operated at 200 W. The XPS data were collected at a takeoff angle of 45°. The survey spectra and high-resolution spectra of the C_{1s} were acquired.

Preparation of alumina gel films

Al(O-sec-Bu)$_3$ (2.47 g, 10 mmol) was mixed with isopropyl alcohol (6.0 g, 100 mmol), then ethyl acetoacetate (1.31 g, 10 mmol) was added. After stirring overnight, the mixture of isopropyl alcohol and

water (0.72 g water / 6.0 g isopropyl alcohol) was slowly dropped into the above mixture during stirring for hydrolysis of $Al(O\text{-}sec\text{-}Bu)_3$. The resultant alumina sol solution appears clear. Alumina nanoparticle doped alumina sol (40 wt. % alumina nanoparticles with respect to the total alumina content in the mixture) was prepared by mixing 3.29 g of the above sol solution with 68.1 mg alumina nanoparticles (80 nm) and sonicating for 5 min. The newly prepared alumina sol was spin-coated onto glass plates (1 cm×2.6 cm) under a rotational speed of 2000 rpm and a holding time of 1 min, then heat-treated at 400°C for 10 min to get the gel films. Nanostructures on the alumina gel surfaces were created by immersing the gel films in boiling water for 5 min and then heating at 400 °C for 10 min.

Self-assembly of FDPA on alumina gel film surfaces

The alumina gel coated glass plates were immersed in 5 mL FDPA solution (1 mM in ethanol) at room temperature. After a certain time, the plates were taken out and rinsed 6 times with fresh ethanol by hand agitation for 30 s. Then the modified chips were blow-dried with N_2, and heated at 120 ^{o}C for 30 min under vacuum to enhance the interaction between alumina surface and the phosphonic acid groups.

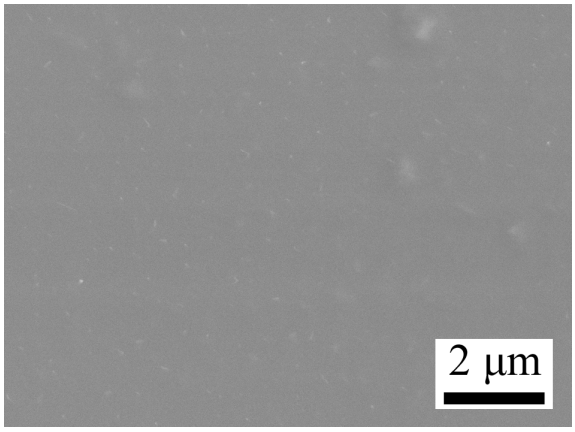

Fig. S1 SEM image of undoped alumina gel film before immersion in boiling water.

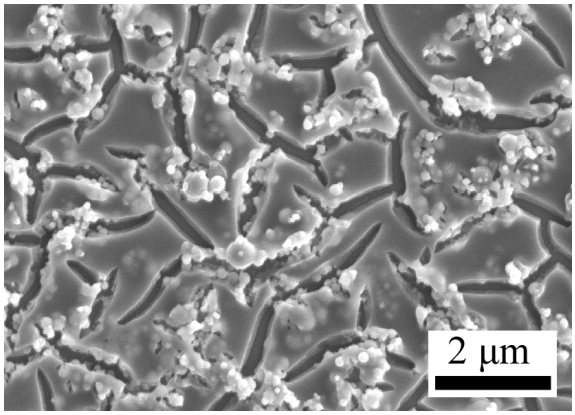

Fig. S2 SEM image of alumina nanoparticles doped alumina gel film before immersion in boiling water.

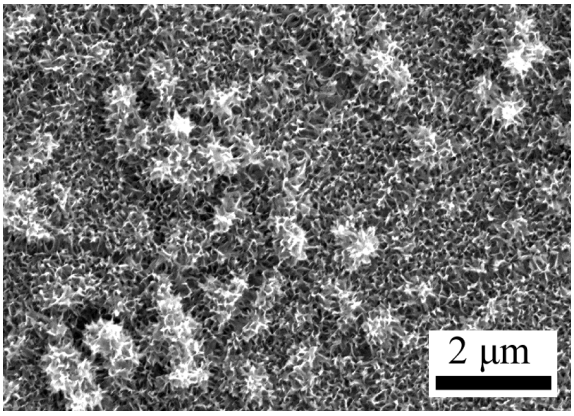

Fig. S3 SEM image of alumina nanoparticles doped alumina gel film after immersion in boiling water.

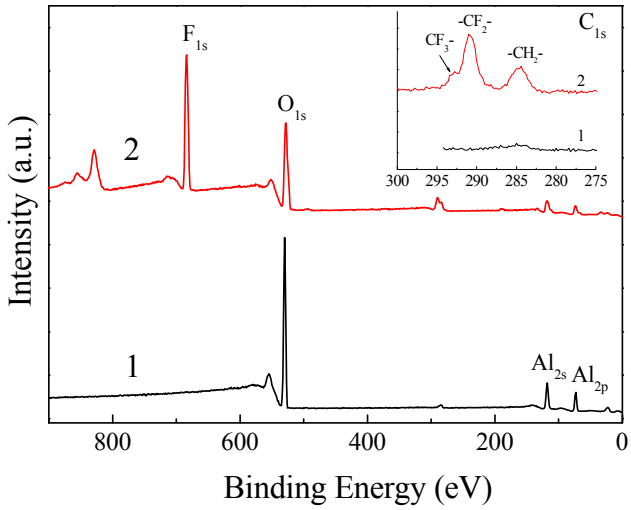

Fig. S4 XPS spectra of the alumina gel film before (1) and after (2) modifying with FDPA.

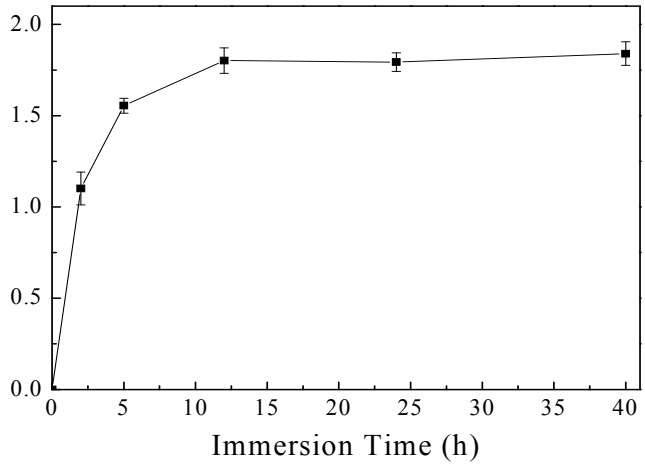

Fig. S5 Time dependence of F/Al ratio on alumina gel film obtained from XPS analysis.

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Movie S1 Process for a 5 μL water drop attaches on the FDPA modified undoped alumina gel film after immersion in boiling water.

Movie S2 Process for a 8 μL water drop departs the FDPA modified hierarchically micro/nanostructured alumina gel surface.

Movie S3 Process for a 10 μL water drop rolls off on the FDPA modified hierarchically micro/nanostructured alumina gel surface.

Movie S4 Process for water drops (*ca.* 9 μL, dropping from a needle close to the surface) slide away on the FDPA modified hierarchically micro/nanostructured alumina gel surface.

Movie S5 A video for the repetitive contact, compression, and release of FDPA modified hierarchically micro/nanostructured alumina gel surface on a supported water droplet.