Electronic Supplementary Information (ESI)

Perfluoropolyether-infused nano-texture: a versatile approach to omniphobic coatings with low hysteresis and high transparency

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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 was purchased from WAKO Pure Chemical Industries. 1*H*,1*H*,2*H*,2*H*-perfluorodecylphosphonic acid (FDPA) was purchased from DOJINDO Laboratories. Perfluoropolyether (PFPE), Fomblin® Y, with average molecular weight of 1800 g/mol was purchased from Sigma-Aldrich. Fluorescence decorated bovine serum albumin (FITC-BSA) was purchased from Sigma-Aldrich. Phosphate butter saline (PBS, 0.01 M, pH 7.2-7.4) was purchased from WAKO Pure Chemical Industries.

Fabrication and surface modification of the nano-textured 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-*sec*-Bu)$_3$. The resultant alumina sol solution appears clear. The newly prepared alumina sol was spin-coated onto silicon or glass plates 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. Nano-texture 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.

For surface modification, the alumina gel coated silicon or glass plates were immersed FDPA solution (1 mM in ethanol) at room temperature. After 24 h, 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.

Preparation of PFPE-infused alumina nano-texture

PFPE liquid was dropped onto the nano-textured alumina gel film. The liquid gradually spread onto the whole substrate. When little amount of PFPE was used, the spreading process is very slow. In this case, the process can be facilitated by gas blowing. The thickness of the coated PFPE layer was controlled by liquid volume.

BSA adsorption test

The BSA adsorption test was performed by submerging the substrates in a 20 μg/mL BSA solution which was prepared with 0.01 M PBS with pH 7.2-7.4. The substrates were immersed for 150 min at room temperature, followed by rinsing with deionized water.

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 AFM image was taken with a SPI3800N probe station (Seiko Instruments Inc., Japan) operated in a dynamic force mode. The static, advancing, and receding contact angles were measured on an Attension Theta system (KSV Instruments Ltd.). Micrographs of hexadecane drops 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. Adsorption of the FITC-BSA was visualized using a fluorescence microscope (Zeiss LSM 510).

Estimation of surface free engineering

The surface free energy was estimated using Owens-Wendt equation[1]:

$$(1+\cos\theta)\gamma_{LV} = 2(\gamma_{SV}{}^{d}\gamma_{LV}{}^{d})^{1/2} + 2(\gamma_{SV}{}^{p}\gamma_{LV}{}^{p})^{1/2}$$

The surface free energy γ_{SV} consists of the dispersion force ($\gamma_{SV}{}^{d}$) and the polar force ($\gamma_{SV}{}^{p}$) components. $\gamma_{SV} = \gamma_{SV}{}^{d} + \gamma_{SV}{}^{p}$

Therefore, the surface free energy can be calculated by the contact angles of two types of liquids with different $\gamma_{LV}{}^{d}$ and $\gamma_{LV}{}^{p}$ values. Herein, we used water (γ_{LV} = 72.80, $\gamma_{LV}{}^{d}$ = 21.80, $\gamma_{LV}{}^{p}$ = 51.00 mN/m) and diiodomethane (γ_{LV} = 50.80, $\gamma_{LV}{}^{d}$ = 49.50, $\gamma_{LV}{}^{p}$ = 1.30 mN/m) as the probe liquids.[2] Contact angles of water and diiodomethane on the PFPE-infused omniphobic surface are 123.0° and 103.3°, respectively. Consequently, the surface free energy of PFPE-infused omniphobic surface was determined to be γ_{SV} = 7.5 mN/m.

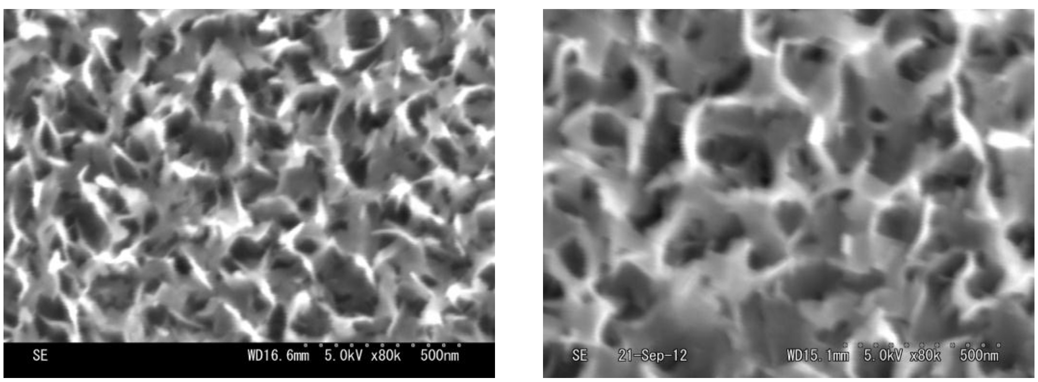

Fig. S1 SEM images of the nano-textured alumina gel surfaces before (left) and after (right) surface modification with FDPA.

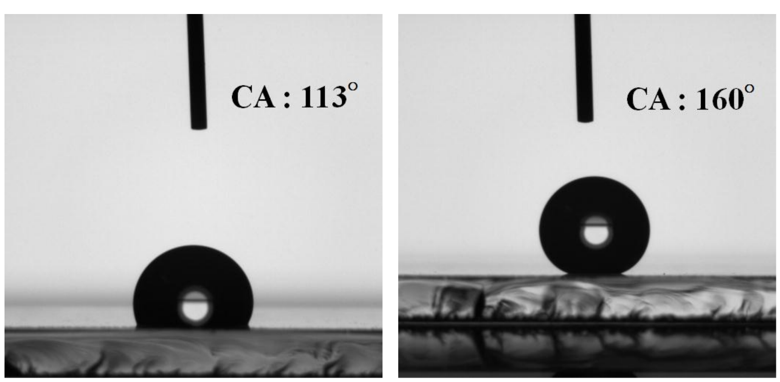

Fig. S2 Images and contact angles of water drops on FDPA-modified flat (left) and nano-textured (right) alumina gel surfaces.

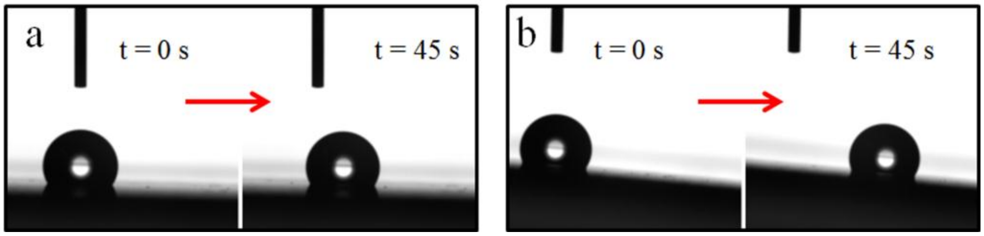

Fig. S3 Micrographs showing the mobility of water drops (3 μL) on the PFPE-infused omniphobic surface that is tilted by 2° (a) and 5° (b).

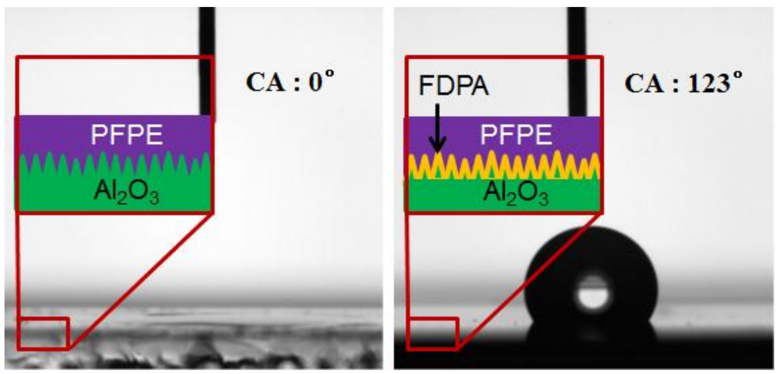

Fig. S4 Images and contact angles of water drops on PFPE-infused alumina nano-texture before (left) and after (right) surface modification with FDPA. Insets show the schematic surface structures.

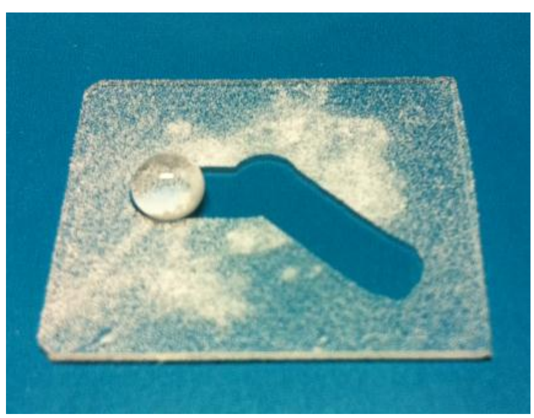

Fig. S5 Photograph of a water drop cleaning $CaCO_3$ particles (10μm) covered omniphobic glass infused with PFPE.

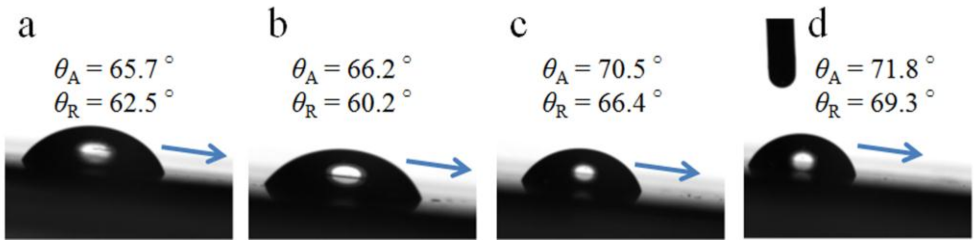

Fig. S6 Advancing (θ_A) and receding (θ_R) contact angles of acetone (a; 10 μL), THF (b; 10 μL), toluene (c; 5 μL), and hexadecane (d; 3 μL) on the PFPE-infused omniphobic surface that is tilted by 5°. Arrows in the images indicate the slipping direction of the droplets.

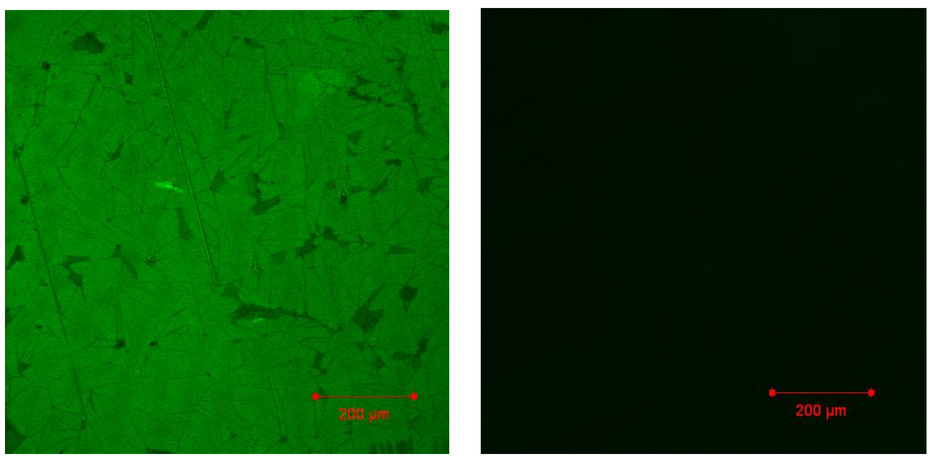

Fig. S7 Fluorescence microscopy images of BSA adsorption on FDPA-modified alumina nano-texture before (left) and after (right) being infused with PFPE. The green color indicates the adsorption of BSA which was decorated with FITC.

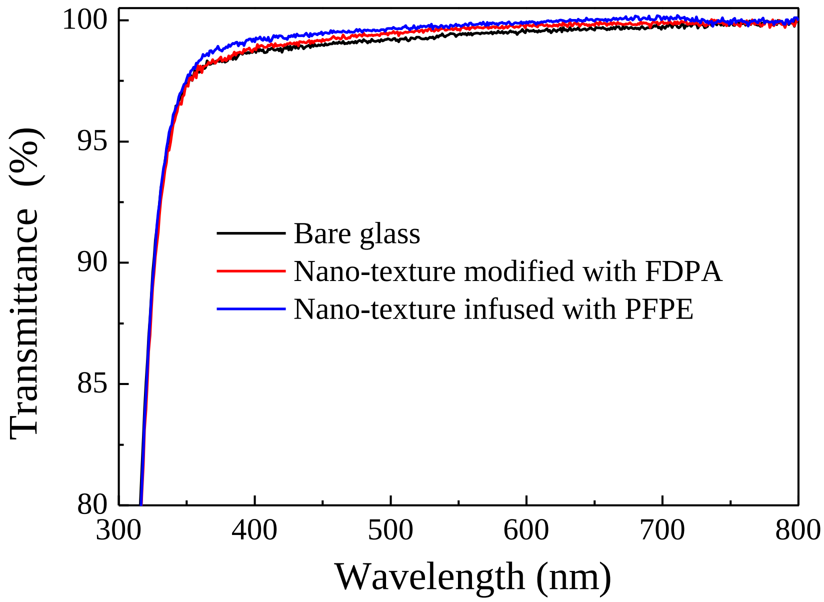

Fig. S8 Transmission spectra of PFPE-infused (blue) and uninfused (red) FDPA-modified alumina nano-texture coated glasses and compared with bare glass (black).

References:

1. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.,* 1969, **13**, 1741.

2. M. Kobayashi, Y. Terayama, H. Yamaguchi, M. Terada, D. Murakami, K. Ishihara and A. Takahara, *Langmuir*, 2012, **28**, 7212.