Supporting Information

Long Perfluoroalkyl Chains Are Not Required For Dynamically Oleophobic Surfaces

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Materials and Methods

Materials

Isopropanol (IPA), 0.01M hydrochloric acid (HCl), ethanol, *n*-hexadecane, *n*-dodecane, and *n*-decane were purchased from Wako Pure Chemical Industries Ltd. TMOS was purchased from Tokyo Kasei Kogyo Co. Ltd. (3,3,3-trifluoropropyl)trimethoxysilane (FAS3, $CF_3CH_2CH_2Si(OCH_3)_3$) and (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FAS17, $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$) were purchased from Gelest Inc. All chemicals were used as received.

Preparation of FAS-TMOS hybrid films

Hybrid films were prepared through conventional co-hydrolysis and co-condensation according to a previously described process (Ref.1-3). Each FAS reagent (FAS3 and FAS17) and TMOS mixture were co-hydrolysed and co-condensed in an IPA/HCl solution for 24 h at 25 ± 2 °C. In this study, the Si/C ratio ($R_{Si/C}$) of the reaction mixture was in the range of 0.5 to 3 so as to tune the surface fluorine concentration. The molar ratio of precursor solution was as follows: Si-OR/IPA/H_2O/HCl = $1:6.3:1:1.8\times10^{-4}$ (see Table S1 for composition for each samples). The precursor solutions were then spincoated on an UV/ozone-cleaned glass (24×48 mm^2) or Si (10×20 mm^2) substrate at 1000 rpm for 5 s and 2000 rpm for 10 s at 25 ± 2 °C and under relative humidity of 40% ± 5. The samples were then dried under vacuum at 60 °C for 24 h. As a control experiment, silsesquioxane films of FAS3 (FAS3sil.) and FAS17 (FAS17sil.) were prepared in the same manner (Table S1).

References

1 C. Urata, D. F. Cheng, B. Masheder and A. Hozumi, *RSC Adv.*, **2012**, *2*, 9805.
2 A. Shimojima, Y. Sugahara and K. Kuroda, *J. Am. Chem. Soc.*, **1998**, *120*, 4528
3 M. Hikata, K. Tanaka, T. Nakamura, T. Kajiyama and A. Takahara, *Langmuir*, **2005**, *21*, 7299.

Table S1. Compositions of the precursor solutions used to prepare FAS-TMOS hybrid and FAS sil. films.

Sample	Si/C	FAS (mL)	TMOS (mL)	IPA (mL)	0.01M HCl (mL)
FAS3-TMOS	2.5	0.055	0.28	4.0	0.15
	2.0	0.069	0.27		
	1.5	0.094	0.25		
	1.0	0.15	0.22		
	0.50	0.32	0.12		
FAS3sil.	-	0.55	0	4.0	0.15
FAS17-TMOS	3.0	0.030	0.30	4.0	0.15
	2.0	0.046	0.30		
	1.5	0.061	0.29		
	1.0	0.093	0.28		
	0.50	0.19	0.26		
FAS17sil.	-	1.2	0	4.0	0.15

Characterization

Contact angles (CAs) were measured with a CA meter (Kyowa Interface Science CA-V150). The CAs were collected using several probe liquids (water, *n*-hexadecane, *n*-decane, and *n*-dodecane) at room temperature (25 °C). For static (θ_S) CA measurement, probe liquids (about 3 μL) were placed gently on the samples. For dynamic (advancing (θ_A) and receding (θ_R)) CA measurement, probe liquid droplets (about 3 μL) were added and withdrawn from the surface, respectively. The CA data reported here was determined by averaging the averaged values of three samples (n = 3), which were prepared in independent experiments. Measurements were taken at ~10 different locations on each sample surface. Minimum tilt angles needed to set probe liquid droplets (5 μL for alkane liquids or 10 μL for water) in motion on the samples were measured using a custom-made tilt angle meter. Film thicknesses of all samples were measured by a stylus profiler (Veeco Dektak 6M). UV-vis spectra in the visible range were recorded with a Cary 5000 spectrophotometer (Agilent Technologies Inc.). The morphology of the samples was observed by atomic force microscopy (AFM, XE-100, Park Systems) using a Si probe (Park Systems, 910M-NCHR; spring constant = 42 N/m and response frequency of 330 kHz) in non-tapping mode. X-ray photoelectron spectroscopy (XPS, Shimadzu, ESCA3400) was performed using MgKα radiation. Core-level signals were obtained at the photoelectron takeoff angle of 15° (with respect to the sample surface). The X-ray source was operated at 20 mA and 10 kV. The thermal stability of our samples was studied by thermogravimetric analysis (TGA, TG/DTA220, Seiko Instruments Inc.) and CA measurements. Several samples were put on a hot plate at a certain temperature (maximum 450 °C) for 10 min and then the dynamic CAs measured using n-decane.

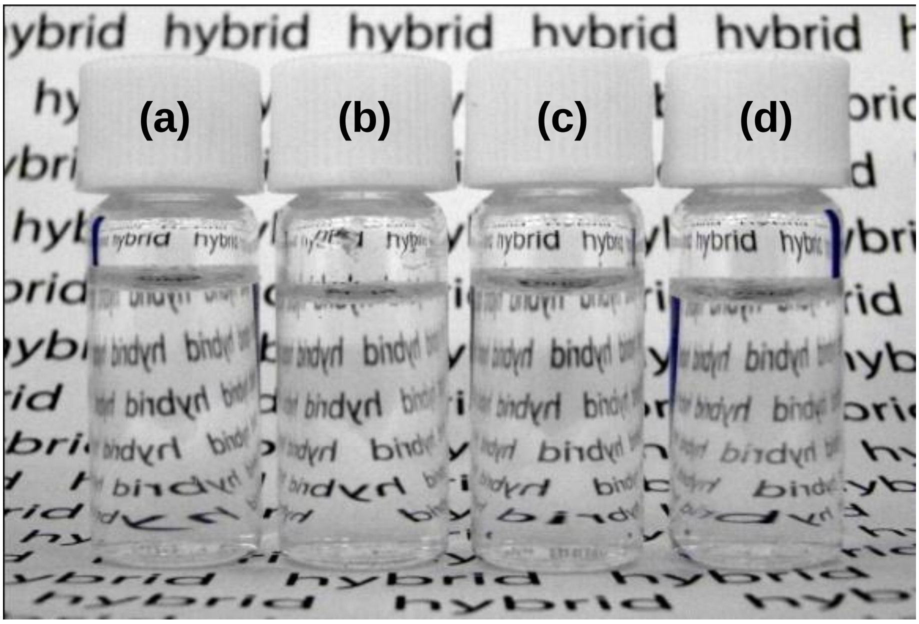

Figure S1. Appearances of precursor solutions of perfluorinated hybrid films. (a) FAS3-TMOS, (b) FAS17-TMOS, (c) FAS3sil., and (d) FAS17sil.

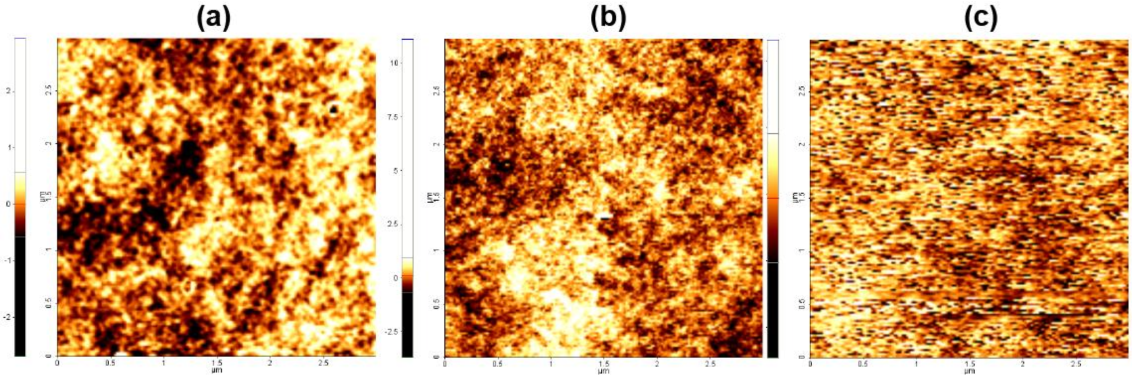

Figure S2. Typical AFM images of (a) FAS3-TMOS hybrid, (b) FAS17-TMOS hybrid, (c) FAS3sil.

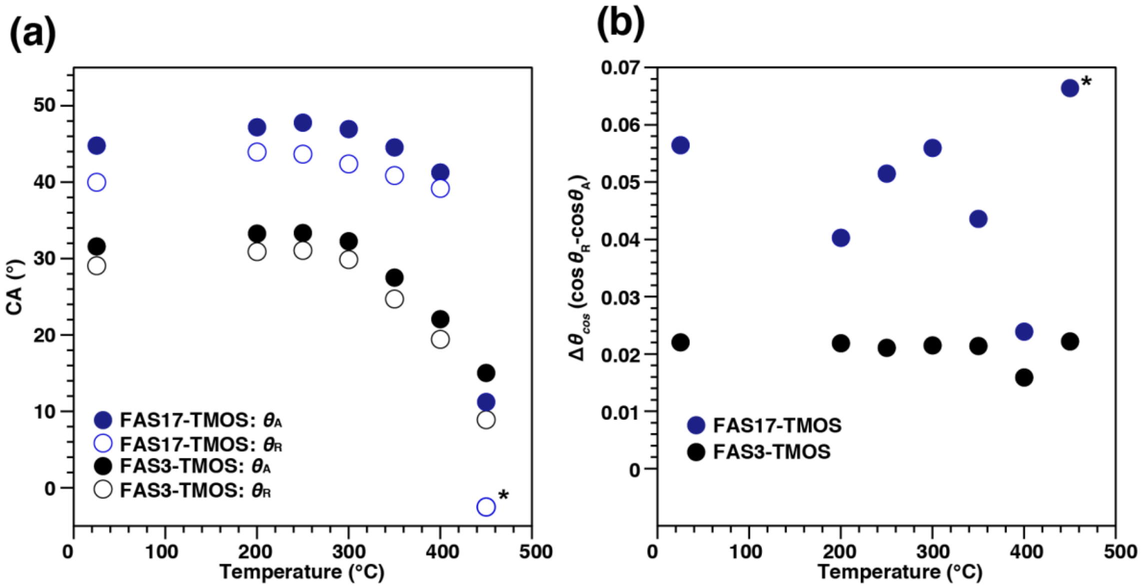

Figure S3. Changes in *n*-decane dynamic CA (a) and CA hysteresis (b) of the samples after thermal treatments at different temperatures (* θ_R could not be obtained.).

Movie S1. Movement of *n*-decane (3 µL) on tilted FAS3-TMOS and FAS17-TMOS film surfaces.