Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Thermally-induced Switchable and Reversible Water Adhesion: Photopatternable Titanate Nanostructures Fabricated on Soft Substrates

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Supporting Methods:

Fabrication of TNT films

Titanium tetraisopropoxide ($Ti(OC_3H_7^i)_4$, TTIP, 95+%), ethanol (EtOH, ≥ 99.5%), and nitric acid (HNO_3, 60 wt.% in water) were purchased from Wako Pure Chemicals Industry Co. Ltd., Japan. The chemicals were used as received.

TNTs films were prepared via a hydrothermal treatment from sol-gel derived amorphous TiO_2 films on various substrates (1.5 cm × 1.5cm), including rutile TiO_2, PP, poly(ethylene terephthalate) (PET), and poly(tetrafluoro ethylene) (PTFE). Briefly, a mixture of deionized water, concentrated nitric acid (HNO_3), and ethanol (EtOH) was added dropwise under stirring at 0 °C to titanium tetraisopropoxide (TTIP) diluted with ethanol. The molar ratio was TTIP/H_2O/EtOH/HNO_3 = 1:1:10:0.2. After 30 min stirring, the sol was coated on the pre-cleaned substrates by spin-coating (3000 rpm, 20 min). The film coated on rutile TiO_2 was hydrothermally-treated in 10 mL of NaOH solutions (0.05 $_M$–1.0 $_M$) at 110 °C for 24 h. Whereas, the films coated on the other substrates were covered with a liquid film of 1 $_M$ NaOH solution (0.3 mL), subjected to 110 °C for 6 h in a closed vessel. The films were washed with deionized water and dried at room temperature. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane was used for FAS coating according to the procedure below.

FAS coating

(Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (Gelest, Inc., USA) was used as FAS for a superhydrophobic treatment. Samples are placed in a closed container together with a small vial containing 100 μL of FAS. The container was then placed in a pre-heated oven at 150 °C for 3 hours.

Synthesis of powdery TNTs

The powdery TNTs were synthesized according to the procedure reported by Kubo et al.[1] TiO_2 (anatase) powders (ST-21, Ishihara Sangyo Co. Ltd., Japan) were hydrothermally treated in an autoclave containing 10 mL of 10 M NaOH solution at 150 °C for 24 h. After the hydrothermal treatment, the product was collected by a suction filtration, followed by washing with deionized water and drying at 50 °C overnight. In the weight loss measurement (Fig. S7), the hydration of powdery TNTs was performed under an ambient air condition for 12h.

Characterization

Nanoarchitectures of TNTs were observed by a field emission scanning electron microscope (FE-SEM; S-4800, Hitachi, Japan, with a thin Au Pt/Pd coating), and a transmission electron microscope (TEM; JEM-2000FX, JEOL, Japan) at operating voltage of 200 kV. Thermogravimetric−differential thermal analysis (TG−DTA; Thermo Plus Evo, Rigaku, Japan) was carried for the powdery TNT sample while continuously supplying N_2 at a ramp rate of 10 °C/min. In the cycle measurement, the temperature was increased to 90° C and then kept for 30 min the temperature. The hydration of powdery TNTs was performed for 12 h under an ambient air condition. Fourier transform infrared spectroscopy (FT-IR: ALPHA FT-IR spectrometer, Bruker Optik GmbH) was employed to analyze decomposition of FAS molecules in the course of UV illumination. Crystal phases of the obtained samples were identified by X-ray diffraction (XRD; SmartLab, Rigaku, Japan) using CuKα radiation (λ = 0.154 nm). Contact angle, θ_{CA}, and sliding angle, θ_{SA}, were measured by a lab-made apparatus. Roughness of the film surface was evaluated with an atomic force microscopy (AFM, SFT−3500, Shimadzu Corp.) equipped with an OMCL-AC-160TS-RS silicon probe.

Supporting Table:

Table S1 NaOH concentration vs root means square roughness of TNT film. Root mean square roughness (RMS) increases with NaOH concentration used for TNT growth.

NaOH concentration /mol·L^{-1}	Root mean square roughness (RMS) /nm
0.05	37.6
0.10	37.0
0.25	42.8
0.50	52.7
0.75	65.4
1.00	72.2

Supporting Figures:

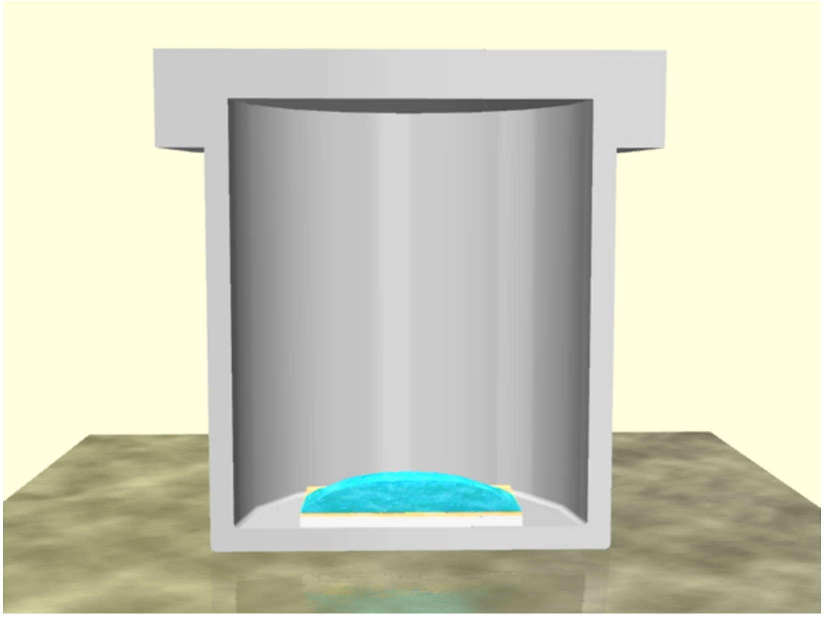

Fig. S1 A schematic image showing the hydrothermal treatment using a NaOH liquid film. The various substrates coated with the amorphous and crack-free TiO_2 film was then covered with a reactive NaOH liquid film. The amount of the liquid (0.3 mL) is large enough to keep hydrothermal condition; 1.3×10^{-3} mol of water is estimated to vaporize in the closed chamber at 110 °C by assuming ideal gas behavior of pure water. The value is much smaller compared to the amount of coated liquid film (1.67×10^{-2} mol).

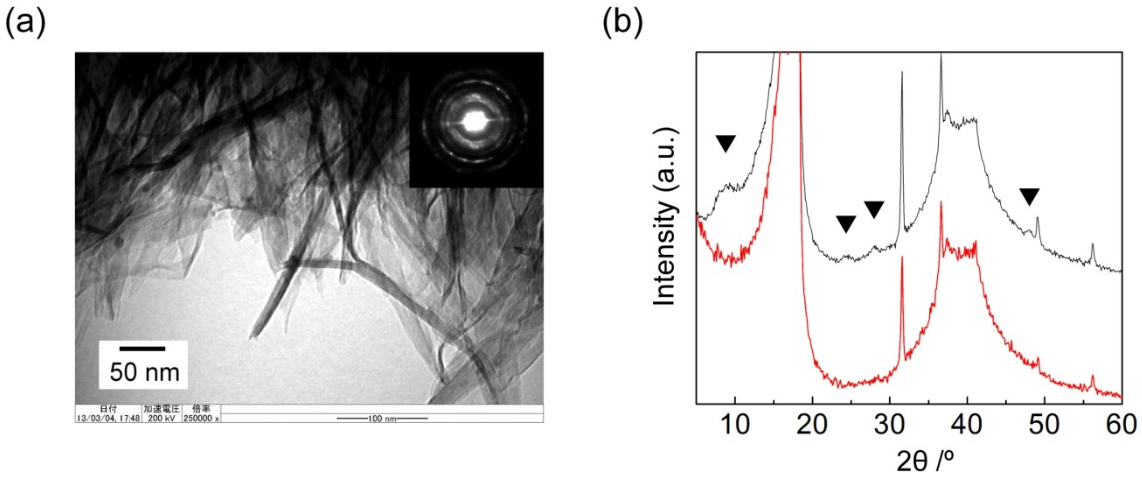

Fig. S2 A TEM image and XRD pattern of TNTs grown on PTFE substrate. (a) The tubular nanoarchitectures are confirmed on the TEM image. The corresponding electron diffraction pattern is represented as an inset. (b) XRD patterns of TNTs grown on PTFE substrate (black line) and a reference PTFE substrate (red line). The peaks indicated (▼) are in good agreement with a previously reported layered titanate structure.[2, 3] All the other peaks are derived from the PTFE substrate.

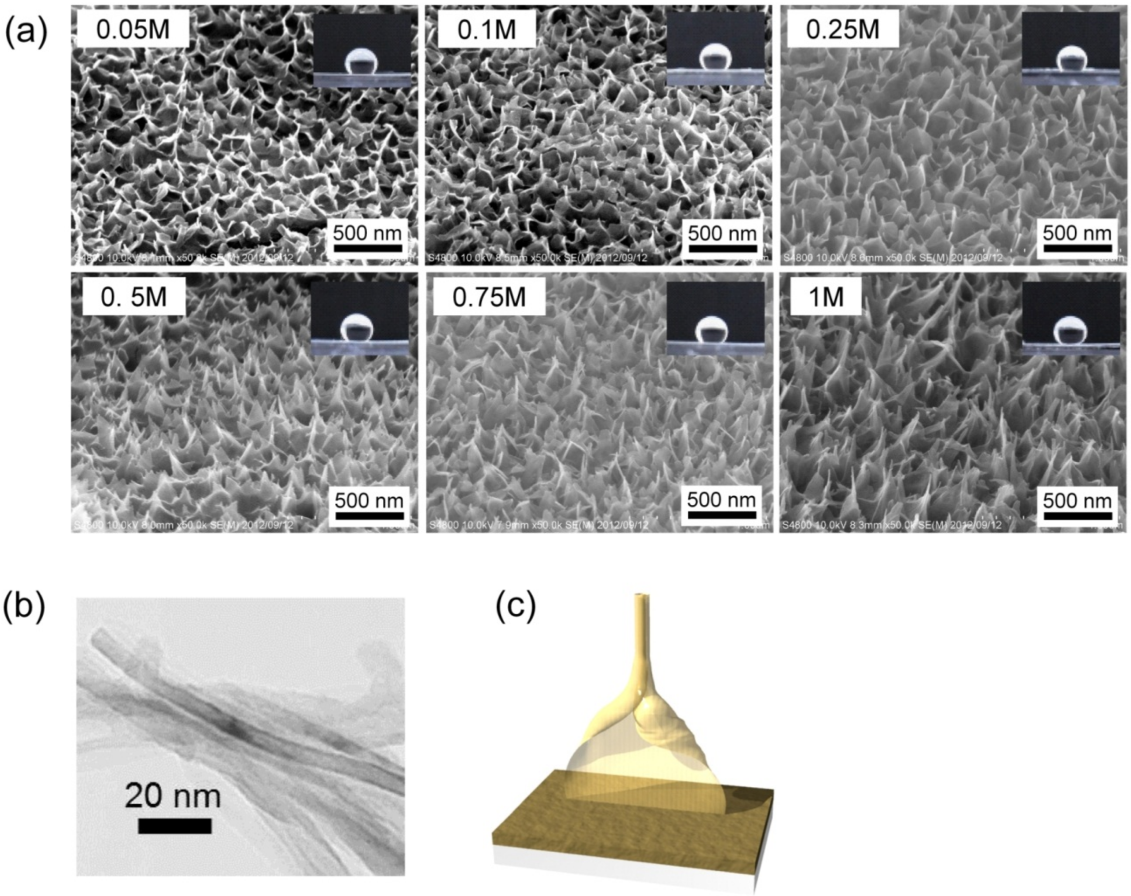

Fig. S3 Variation of FAS-modified TNT nanostructures with the concentrations of NaOH. (a) The increase of NaOH concentration clearly enhances the crystal growth of titanate. Up to 0.25 M of NaOH, titanate nanosheets dominantly form as a nanostructure. Further increasing NaOH produces nanotubes (TNTs) at the top end of nanosheets. (b) A TEM image showing the tubular structure of TNTs. (c) The formation of TNT proceeds by scrolling at a top end of nanosheet.[3] The coatings were made on a rutile TiO_2 substrate.

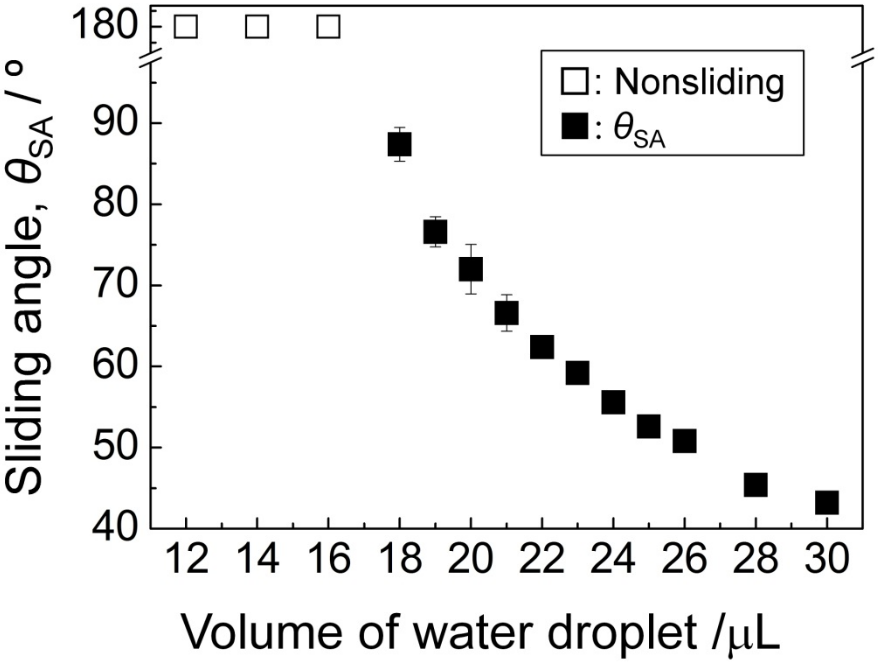

Fig. S4 Sliding angle, θ_{SA} vs volume of water droplet. The measurements were performed on the TNTs film prepared with 1 M NaOH after FAS coating. Substrate: rutile TiO_2.

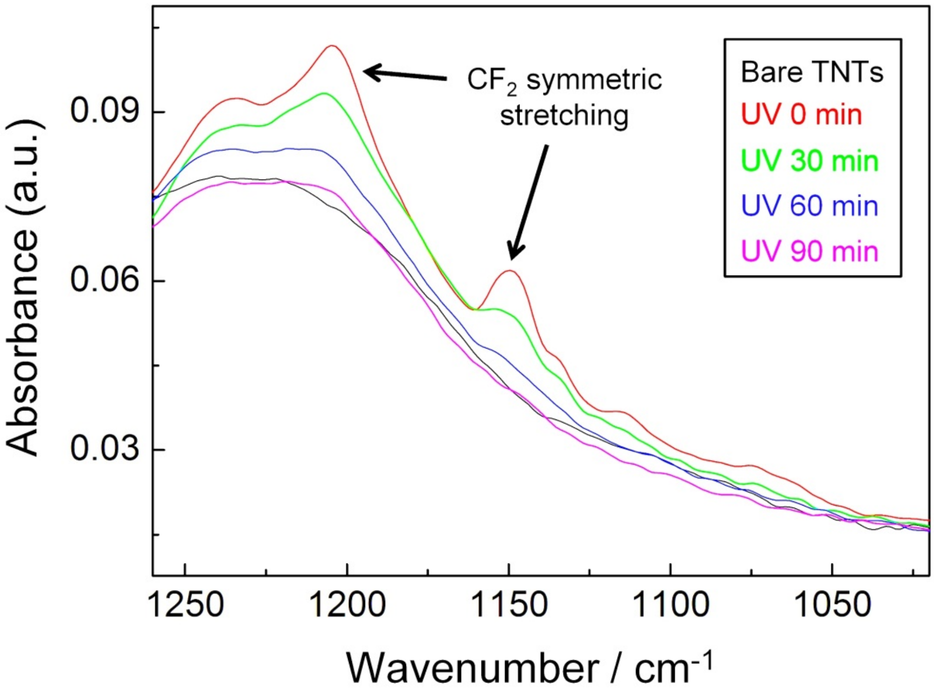

Fig. S5 FT-IR spectra of FAS-modified TNTs with UV illumination time. Absorption bands corresponding to CF$_2$ symmetric stretching disappear with increasing illumination time, suggesting FAS decomposition by UV illumination.[4]

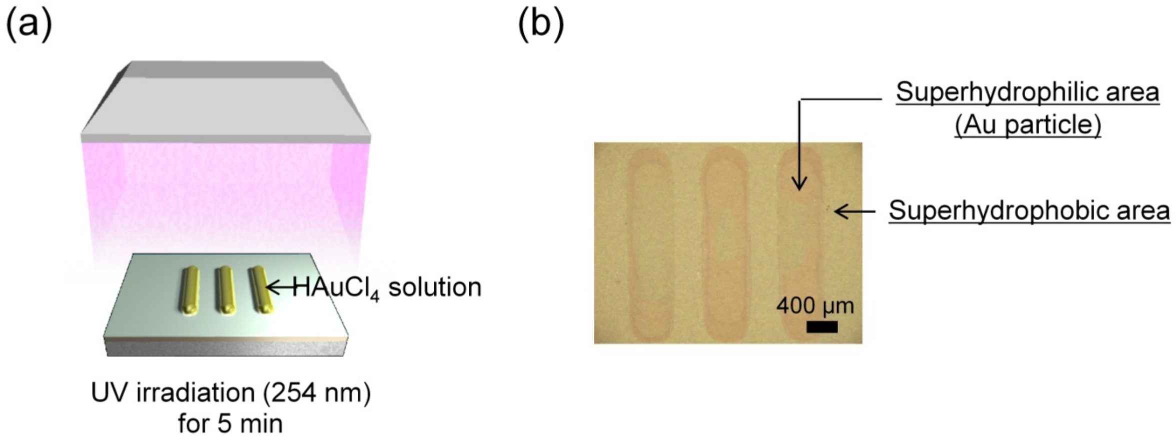

Fig. S6 Selective formation of Au particles on superhydrophilic areas. (a) Scheme of the photochemical reaction. (b) Patterned formation of Au nanoparticles on the TNTs film.

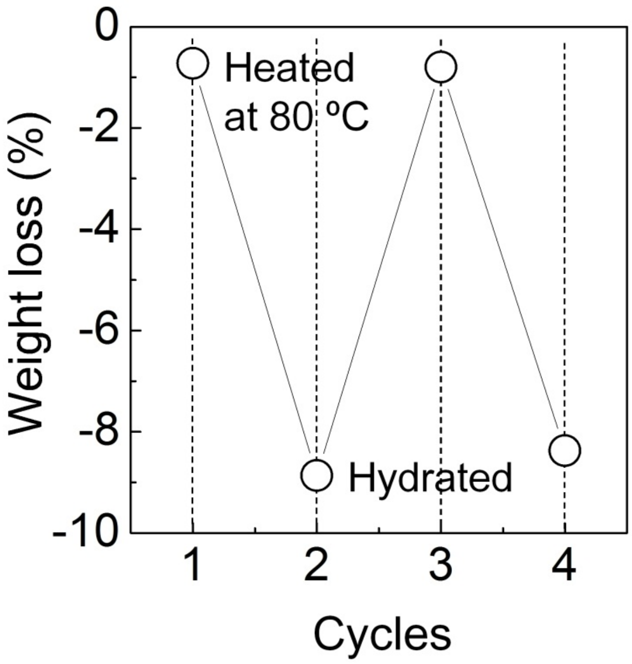

Fig. S7 Weight loss of powdery TNTs at 90 °C in 30 min. Powdery TNTs sample was prepared by the procedure described in Supplementary Method. The analyses were performed as follows: first, the sample was kept at 80 °C for 30 min in an oven and then the weight loss at 90 °C in 30 min was measured by TG-DTA (cycle 1). Subsequently, the sample was hydrated in ambient air condition for 12 h and subjected to the TG-DTA analysis with the same conditions (90 °C in 30 min) (cycle 2). The cycles 1 and 2 were repeated (cycle 3 and 4).

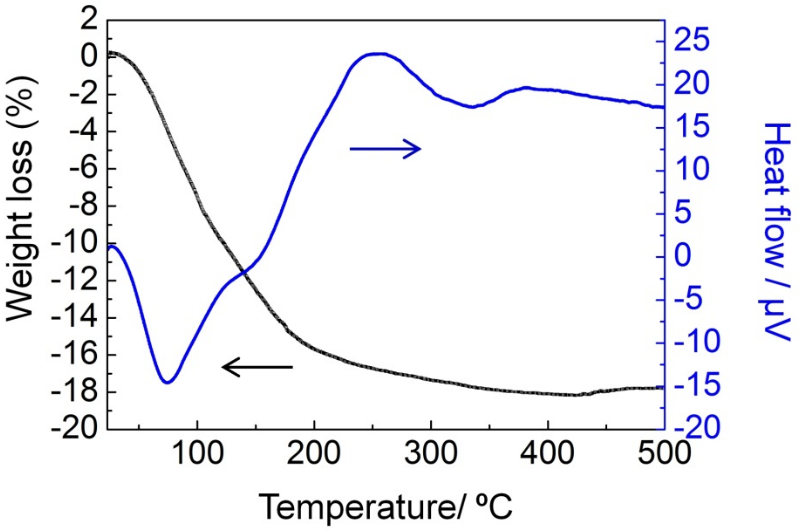

Fig. S8 TG-DTA curves of powdery TNTs. Endothermic weight losses around at 75 and 155 °C are derived from release of water adsorbed on the surface and confined in the interlayer, respectively.

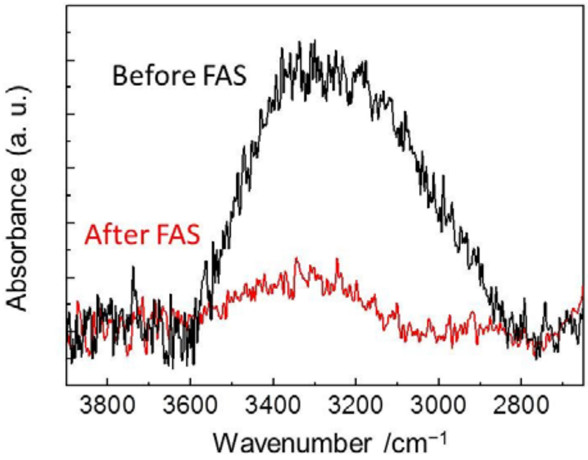

Fig. S9 FTIR spectra of TNT films before and after FAS treatment. The film was measured by ATR configuration.

Video 1

✓ Tilt angle of the film: 1.9 °
✓ Water droplet: 4 μL

Video 2

References

[1] T. Kubo, A. Nakahira, J Phys Chem C 2008, 112, 1658.

[2] A. Nakahira, W. Kato, M. Tamai, T. Isshiki, K. Nishio, H. Aritani, J Mater Sci 2004, 39, 4239.

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[4] K. Teshima, S. Suzuki, K. Yubuta, Y. Sonobayashi, T. Suzuki, T. Shishido, H. Sugimura, S. Oishi, Surf Coat Tech 2008, 203, 812.