Supplementary information for

"Titanate nanofunnel brushes: toward functional interfacial applications",

by Kenji Okada, Yasuaki Tokudome, Paolo Falcaro, Yuichiro Takamatsu, Atsushi Nakahira and Masahide Takahashi

Experimental method

TNF brushes synthesis: polycrystalline rutile TiO_2 plates were prepared by heating titanium plate (1.5 cm × 1.5 cm, The Nilaco Corporation, Japan) at 800 °C for 4 h in an ambient atmosphere. TiO_2 coating sol was prepared by the following process. First, titanium tetraisopropoxide ($Ti(OC_3H_7^i)_4$, TTIP, Wako Pure Chemical, Japan) was diluted with ethanol (EtOH, Wako Pure Chemical, Japan) at 0 ºC. Then, deionized water and nitric acid (Wako Pure Chemical, Japan) diluted with EtOH were added dropwise to the TTIP-EtOH solution under vigorous stirring. The solution was further stirred for 30 min at 0 ºC. The final molar composition of coating TiO_2 sol was TTIP/H_2O/EtOH/HNO_3 = 1:1:10:0.2. The coating sol was deposited on the rutile TiO_2 substrate by spin coating at 3000 rpm for 20 s. Then, the film on the rutile TiO_2 substrate was dried at room temperature. The obtained amorphous TiO_2 thin film on the rutile TiO_2 substrate was hydrothermally-treated in an autoclave containing 10 ml of NaOH aqueous solution at 110 ºC for 24 h. The concentration of NaOH was varied from 0.05 M to 1 M. After the hydrothermal treatment, samples were washed with distiled water and then dried at room temperature.

Characterization: SEM images were obtained by a field emission scanning electron microscope (FE-SEM) (S-4800, Hitachi, Japan). TEM images were obtained by a transmission electron microscope (TEM) (JEM-2000FX, JEOL, Japan) operated at 200 kV. XRD patterns were obtained with a Rigaku multiflex (Rigaku, Japan) using Cu Kα radiation (λ= 1.54 Å) operated at 40 mA and 40 kV.

Hydrophobic surface treatment: (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (Gelest, Inc., USA) was used as FAS for a superhydrophobic treatment. TNF brushes 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 for CVD of FAS on TNF brushes.

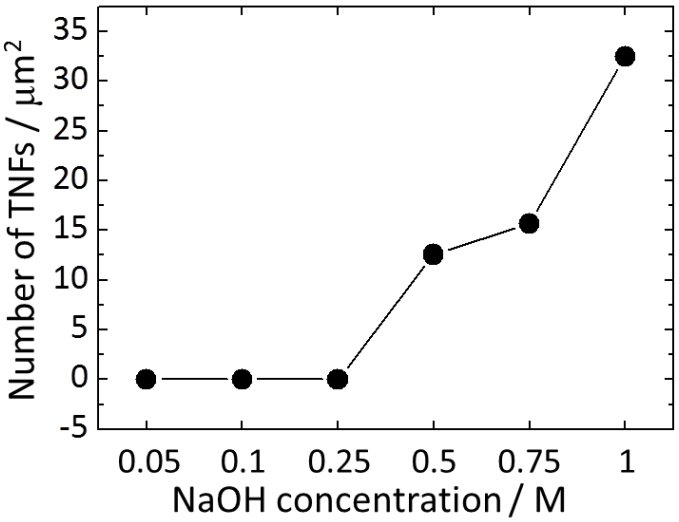

Figure S1. Number of TNFs per unit area against the NaOH concentration under hydrothermal treatment.

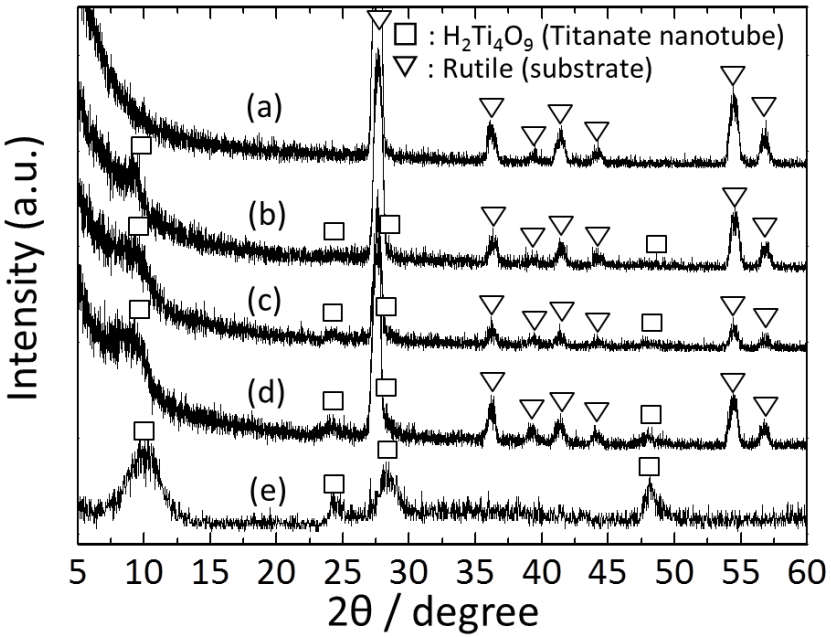

Figure S2. XRD patterns of TNF brushes prepared under different hydrothermal conditions: (a) before hydrothermal treatment (precursory TiO_2 film); (b) 0.1 M NaOH; (c) 0.5 M NaOH; (d) 1 M NaOH. As a reference, titanate nanotubes were synthesized from anatase TiO_2 powder according to the previously-reported protocol[1] and the XRD pattern ascribed to titanate, $H_2Ti_4O_9$, is depicted in (e). Difraction peaks corresponding to rutile phase in (a)-(d) were attributed to rutile under layer.

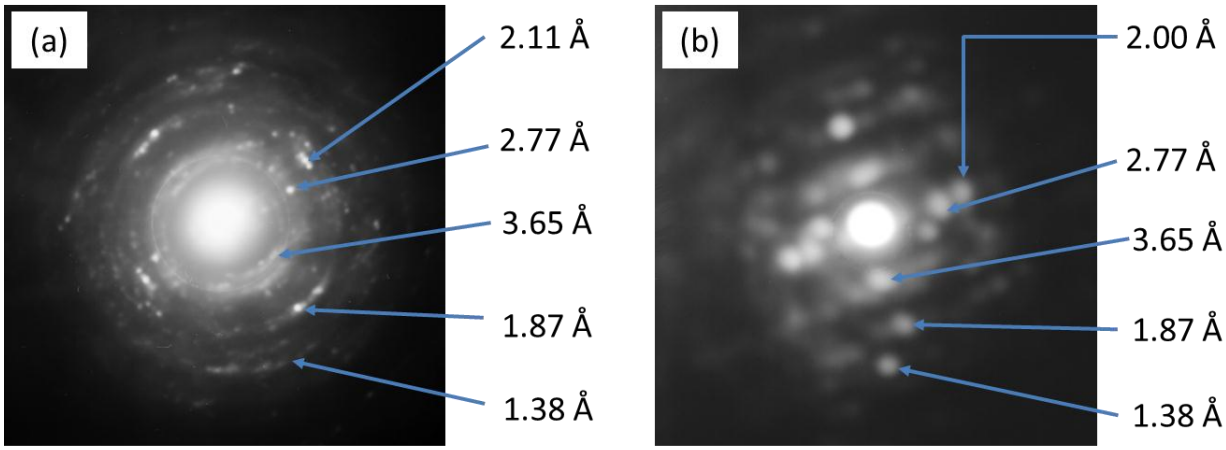

Figure S3. Electron diffraction images of TNF brushes synthesized with (a) 0.5 M and (b) 1 M NaOH concentrations. Corresponding d-values of diffraction spots are shown.

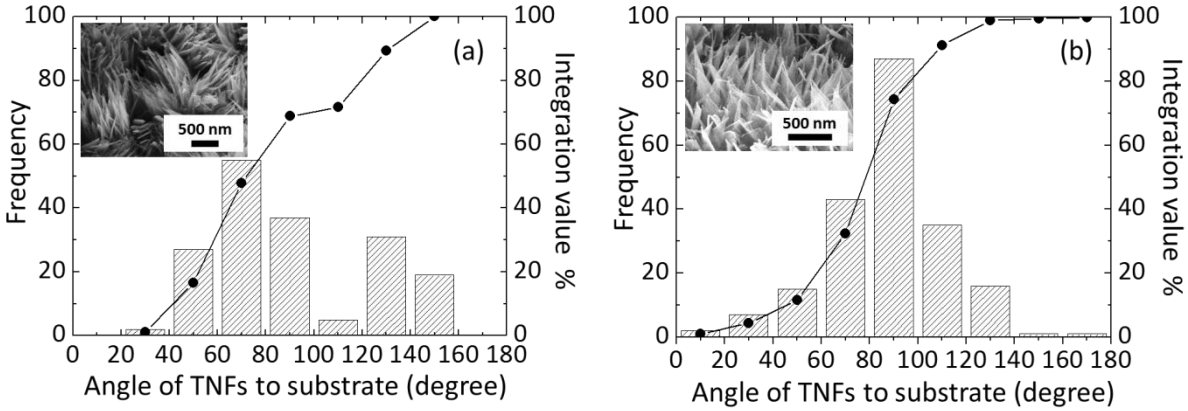

Figure S4. Angle distributions of TNFs to the substrate surface: (a) TNFs grown directly on rutile TiO_2; (b) TNFs grown on amorphous TiO_2 thin film. The insets are SEM images of the corresponding TNFs.

The procedure used to grow TNFs on rutile polycrystalline substrate is here described: a small part of the polycrystalline rutile substrate has been masked using a tape. The substrate has been spin-coated by TiO_2 precursory solution. After removing the tape, the polycrystalline rutile TiO_2 coating is remaining in the masked region. Unmasked region was coated with amorphous TiO_2. Finally, both parts (rutile and amorphous TiO_2 on the same substrate) have been hydrothermally-treated under the same condition. We could grow TNFs on polycrystalline rutile part with the present procedure due to the existence of amorphous coating just besides the rutile part. It should be mentioned that TNFs could not be grown on rutile substrates under the present hydrothermal condition without partial amorphous coating.

Angle distribution[2] of TNFs to the substrate surface is strongly dependent on the crystalline nature of the TiO_2 precursory films. TNFs that grown at polycrystalline rutile part showed a broad distribution of the growth angle (Figure S4(a)). The SEM image shown in the inset of Figure S4(a) and the angle distribution data indicate that TNFs form bundles oriented partially in separated domains. The angle distribution of TNFs to the film surface grown on amorphous TiO_2 thin film part exhibited regularly- and vertically-oriented ones to the film surface (Figure S4(b)).

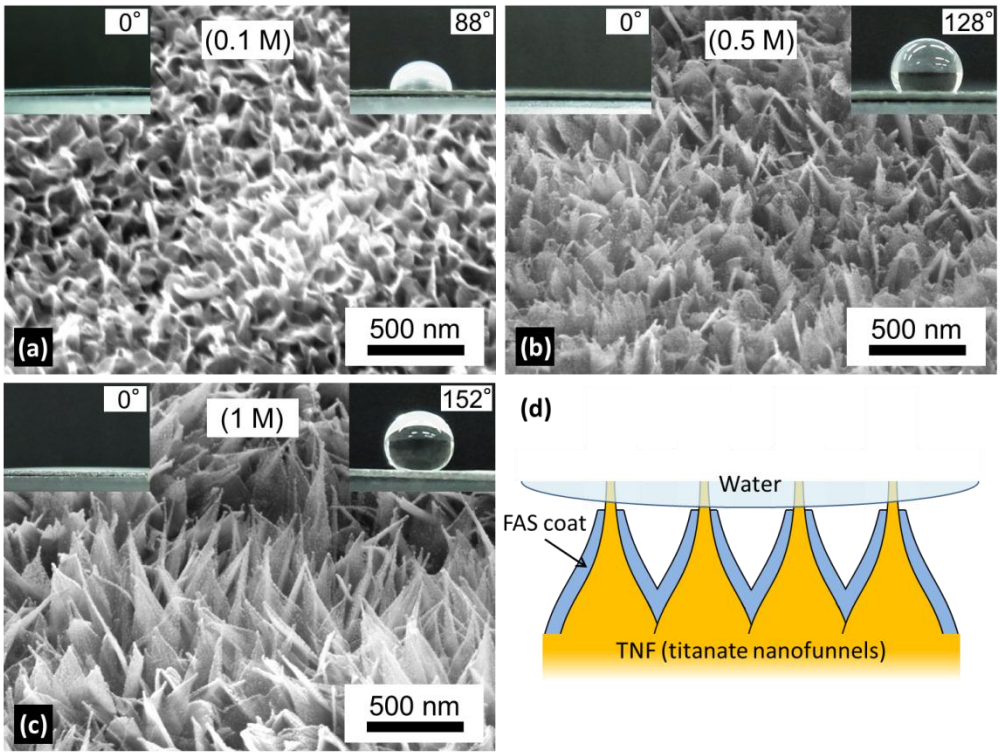

Figure S5. FE-SEM images of TNF brushes synthesized with different NaOH concentrations (observed from 45° tilted angle): (a) 0.1 M, (b) 0.5 M, (c) 1 M. The insets on the left and right top are water droplet shapes with their contact angles (CA) before and after FAS treatment, respectively. (d) Schematic illustration of superhydrophobic adhesive surface of FAS-modified TNF brush.

Figure S5(a)-(c) show relationships between wettability and the surface morphologies of TNF brush. Before FAS treatment, all TNF brushes with different nanostructures show superhydrophilic surfaces (left top insets of Figure S5(a)-(c)). The superhydrophilicity can be attributed to both titanate-derived hydrophilicity and surface nanostructure. After modification of FAS, the surface hydrophobicity changed with the surface morphologies from nanosheets to nanofunnels. This result is explained by the Cassie's equation. At the interfaces between substrate surface and water, the morphology change from nanosheets to nanotubes (the top of nanofunnels) increases the proportion of water/air interfaces, leading to enhancement of the surface hydrophobicity.[3] These hydrophobic surfaces show adhesive property. The formation of adhesive hydrophobic surfaces would be attributed to titanate-derived hydrophilicity of the top nanotube and hydrophobicity of the bottom of nanosheet coated with FAS. (Figure S5(d)).

References

1 T. Kubo and A. Nakahira, *J. Phys. Chem. C*, 2008, **112**, 1658.

2 Angle distributions were estimated from SEM images of samples observed with the tilt angle of 45˚. The angles of respective TNFs to substrate surface were measured on different 176 and 207 TNFs on rutile and amorphous TiO_2 thin film, respectively.

3 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.