Supplementary Information

Thermo-responsive wettability via surface roughness change on polymer-coated titanate nanorod brushes toward fast and multi-directional droplet transport

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Methods

Synthesis of Paraffin/TNR brush: Vertically-aligned titanate nanorod (TNR brush) was prepared on a titanium plate (30 mm × 30 mm × 0.20 mm, The Nilaco Corporation, Japan) via a hydrothermal treatment (20 ml of 1 M NaOH aq. at 110 ºC for 24 h). After the hydrothermal treatment, the samples were washed with distilled water and then dried at 70 ºC. Then, the surface of TNR brush was modified with octyltrimethoxysilane (OTMS, 96 %, Merck KGaA, Germany) by chemical vapor deposition. TNR brush was placed in a closed container together with a small vial containing 100 μL of OTMS. The container was then placed in a pre-heated oven at 130 °C for 3 h for OTMS modification. Paraffin coating (Melting-point: 42 – 44 ºC, FUJIFILM Wako Pure Chemical Corporation, Japan) on the OTMS-modified TNR brush was conducted by spin-coating of the paraffin-isooctane solution (50 g/L) at 2000 rpm for 120 s. As a reference sample, a paraffin-coated flat surface (paraffin-coated glass) was prepared by a same procedure for OTMS modification and paraffin coating.

Characterization: The surface morphologies were observed by a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) and an atomic force microscope (AFM, SFT-3500, Shimadzu, Japan). Contact angle, θ_{CA}, was measured with a contact-angle goniometer (DMs-401, Kyowa interface Science Co. Ltd.) using 11 μL of a water droplet. Fourier transform infrared spectroscopy in ATR mode (FT-IR: ALPHA FT-IR spectrometer, Bruker Optik GmbH) was employed to confirm surface modification by OTMS and paraffin-coating.

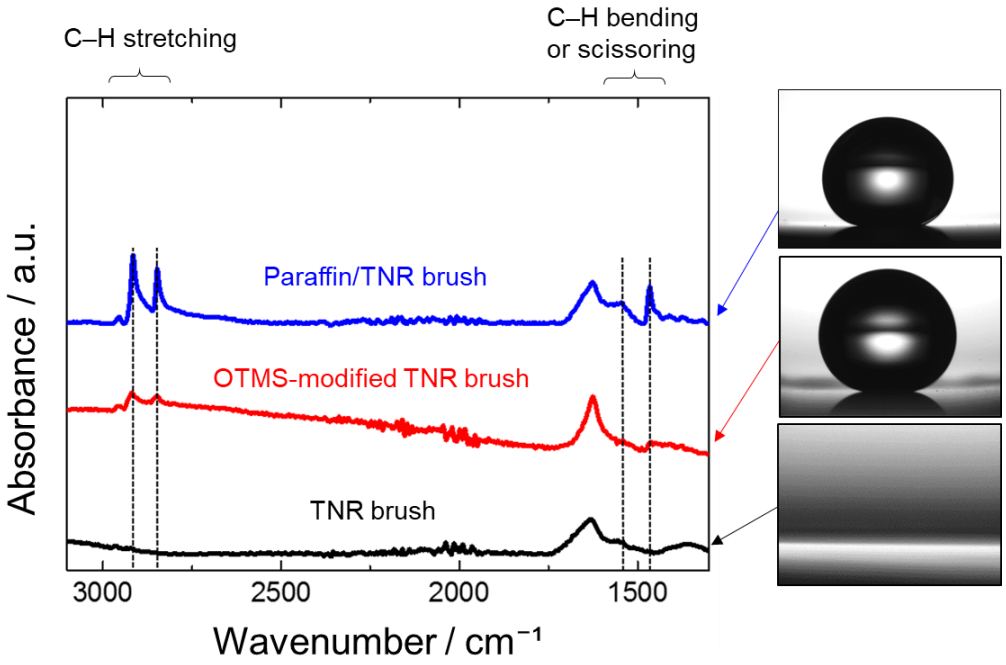

Figure S1. FT-IR spectra of pristine TNR brush, OTMS-modified TNR brush and Paraffin/TNR brush. Photos of water droplets on the surfaces are also shown.

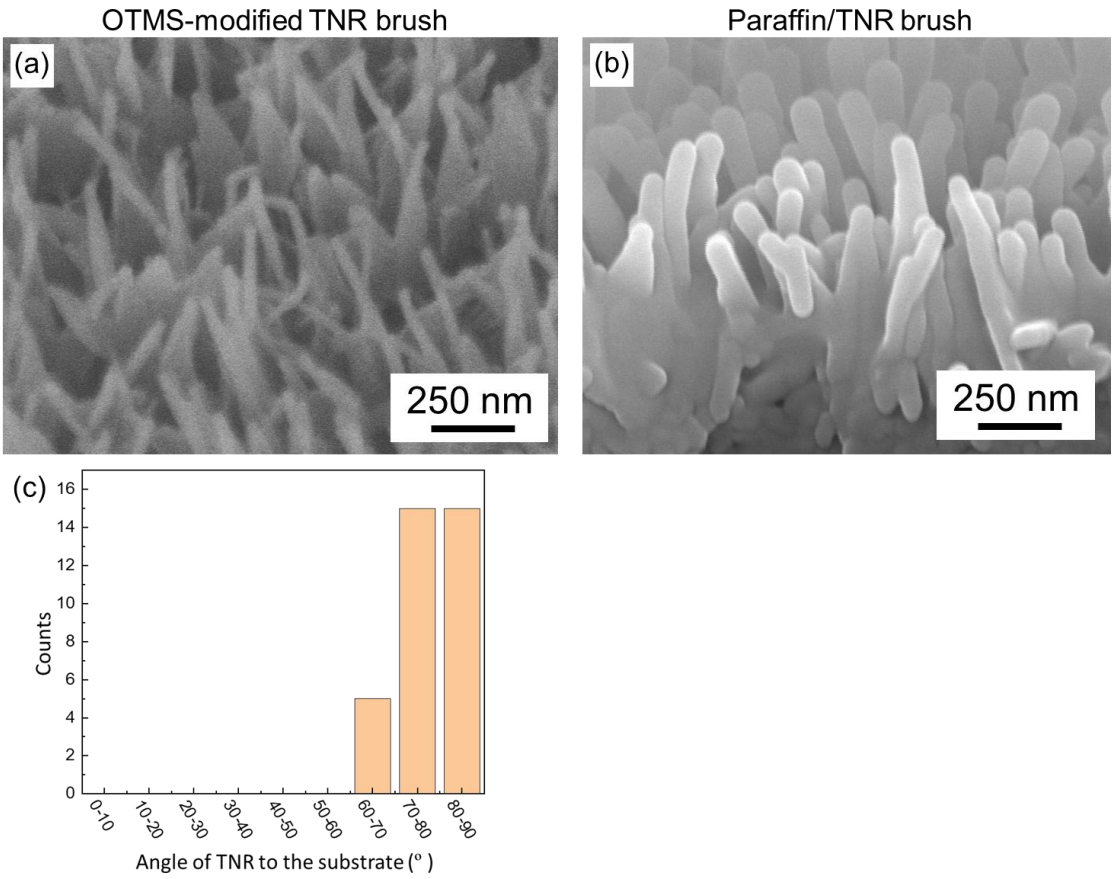

Figure S2. SEM images of (a) OTMS-modified TNR brush and (b) Paraffin/TNR brush. (c) The distribution of the angle of titanate nanorods with respect to the substrates.

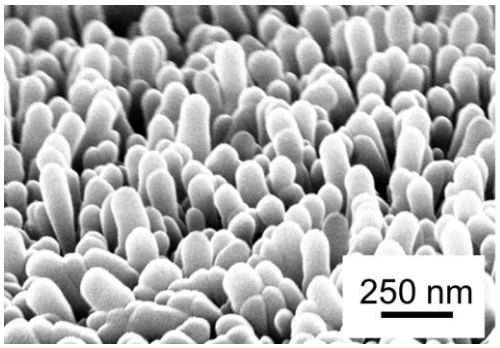

Figure S3. SEM image of Paraffin/TNR brush after 10 cycles of reversible heating/cooling (at 33 and 60 ºC) process.

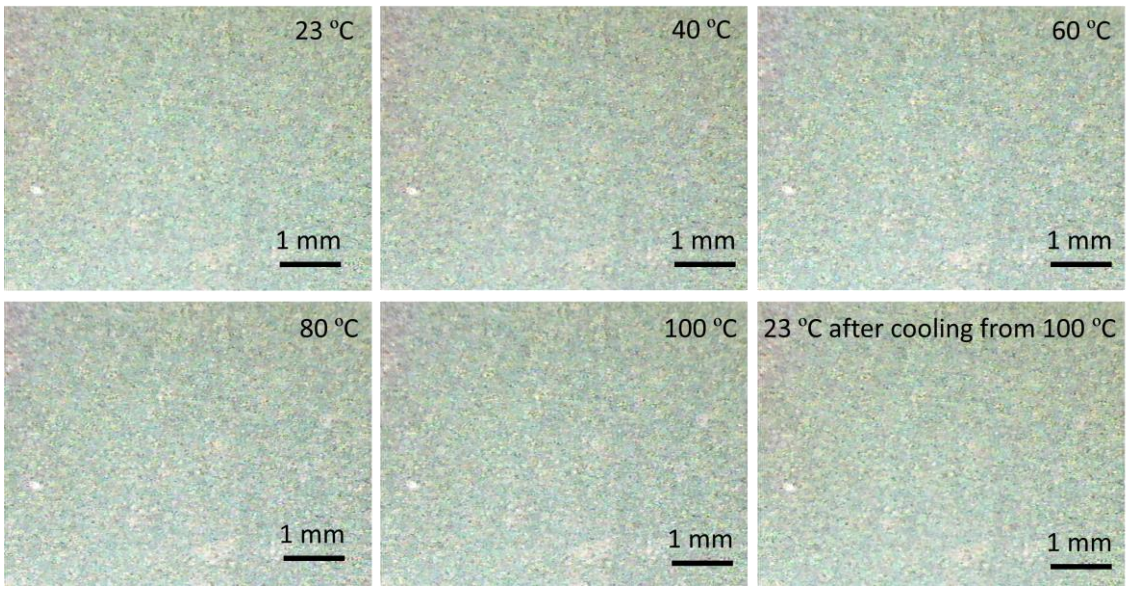

Figure S4. In-situ optical microscope observations of the Paraffin/TNR brush at temperatures of 23 (before and after heating to 100 ºC), 40, 60, 80 and 100 ºC.

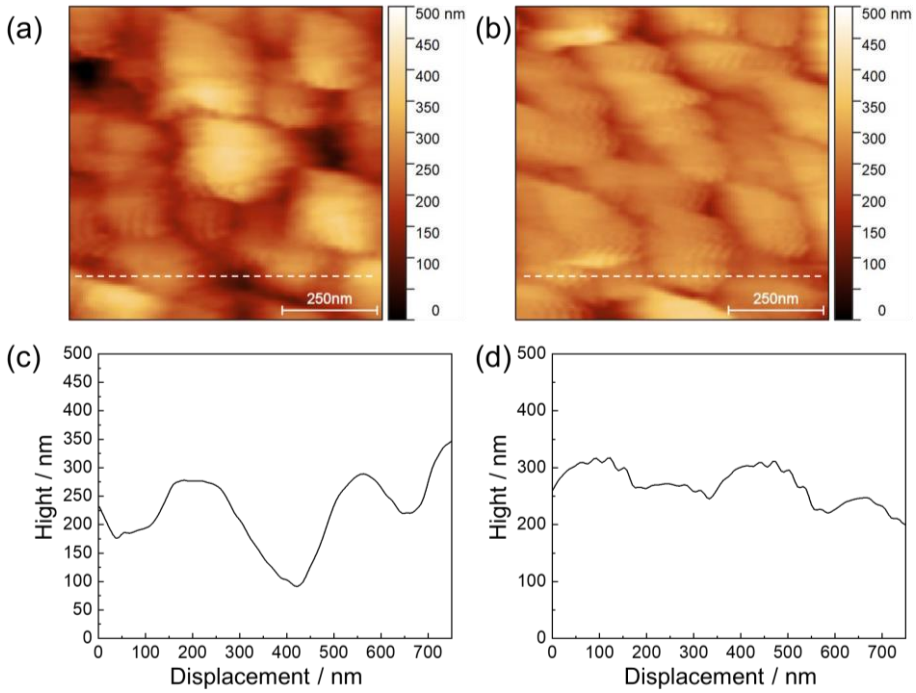

Figure S5. Atomic force microscope (AFM) images of the Paraffin/TNR brush at (a) ~26 ºC and (b) ~55 ºC. (c and d) The line profiles were obtained on the while dot lines of (a) and (b), respectively. Root mean square roughness (RMS) for Paraffin/TNR brush at ~26 and ~55 ºC was calculated as

68±17 and 39±14 nm from the AFM profiles, respectively.

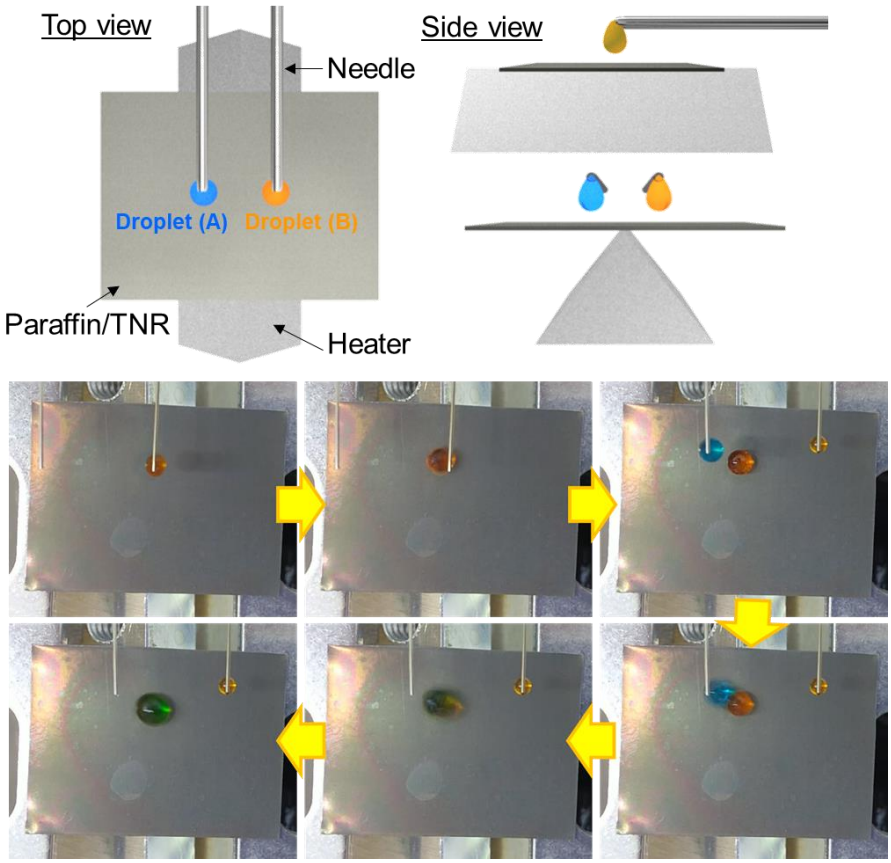

Figure S6. Droplet mixing on the Paraffin/TNR brush. The orange droplet (15 µL of 1.8 mM methyl orange) falls 3 mm away from the heated part on the right side, and then the blue droplet (15 µL of 3.4 mM methylene blue) falls 3 mm away from the heated part on the left side. The blue droplet mixed with the orange droplet in 0.04 s.

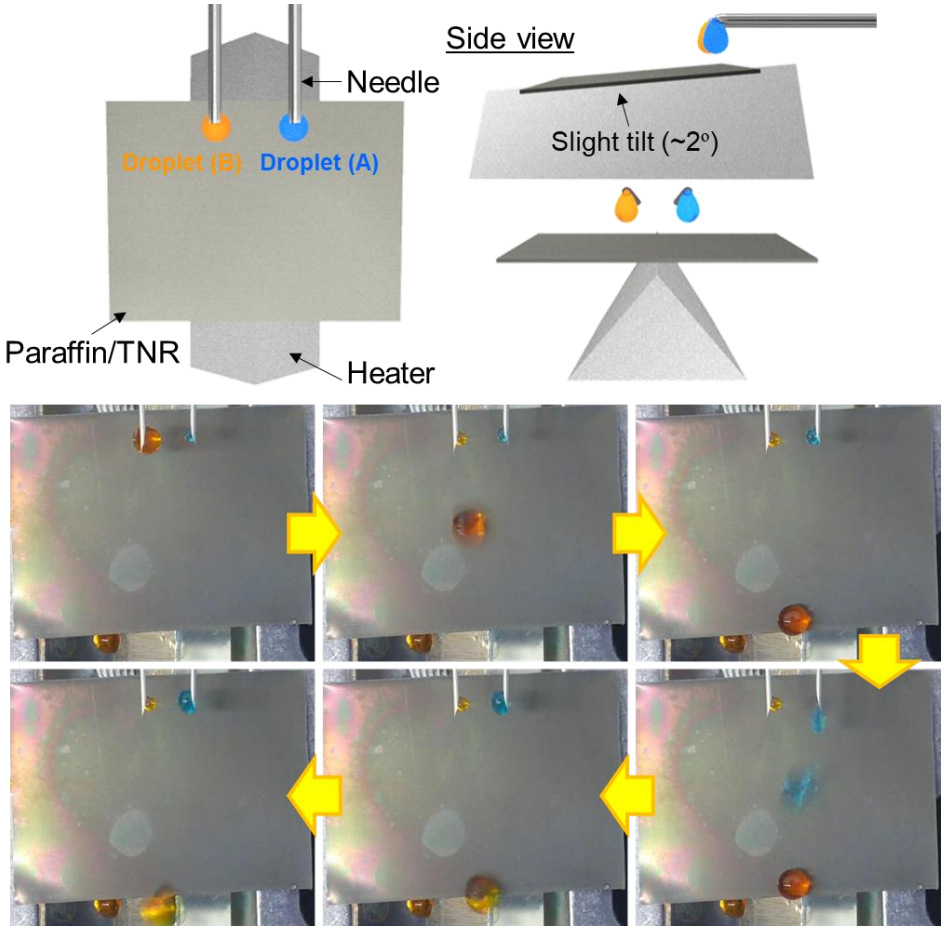

Figure S7. Droplet mixing and collection on the Paraffin/TNR brush in which the Paraffin/TNR brush was slightly tilted. The orange droplet (15 μL of 1.8 mM methyl orange) falls 3 mm away from the heated part on the right side. The orange droplet stopped at the part at the edge of surface. Then, a blue droplet (15 μL of 3.4 mM methylene blue) falls 3 mm away from the heated part on the left side. The blue droplet mixed with the orange droplet and fell off the substrate in 0.04 s, and the mixed droplet was collected under the substrates.