

## Electronic Supplementary Information (ESI)

# Bio-Inspired Fabrication of Superhydrophobic Surfaces through Peptide Self-Assembly

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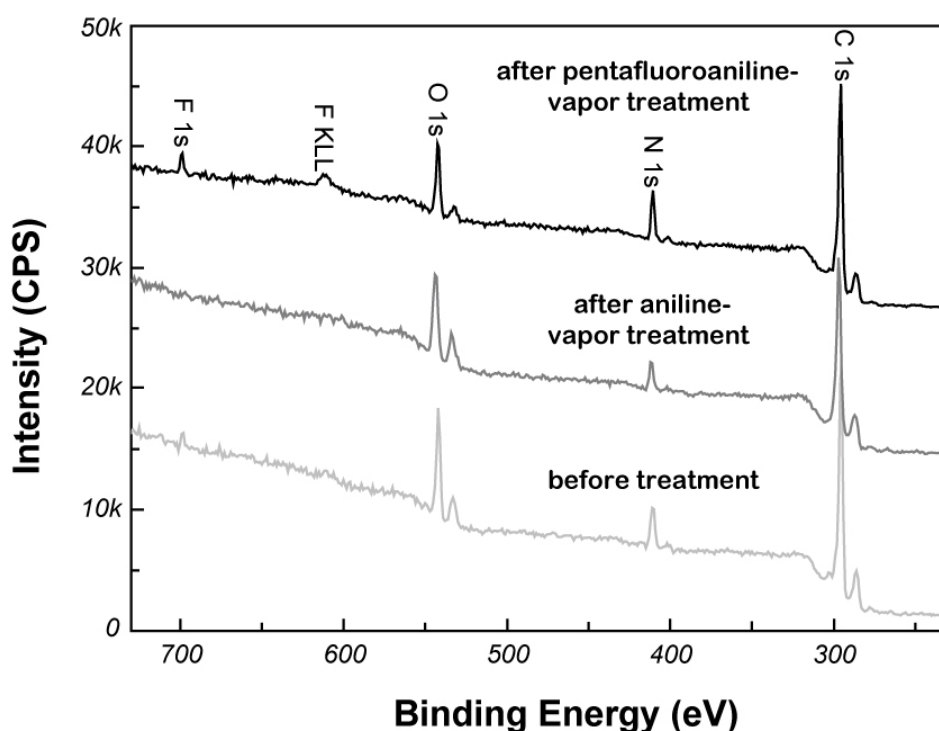
## Experimental Methods

*Materials:* Diphenylalanine in a lyophilized form was obtained from Bachem AG (Bubendorf, Switzerland). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), aniline, and 2,3,4,5,6-pentafluoroaniline were purchased from Sigma-Aldrich Co. (St. Louis, MO).

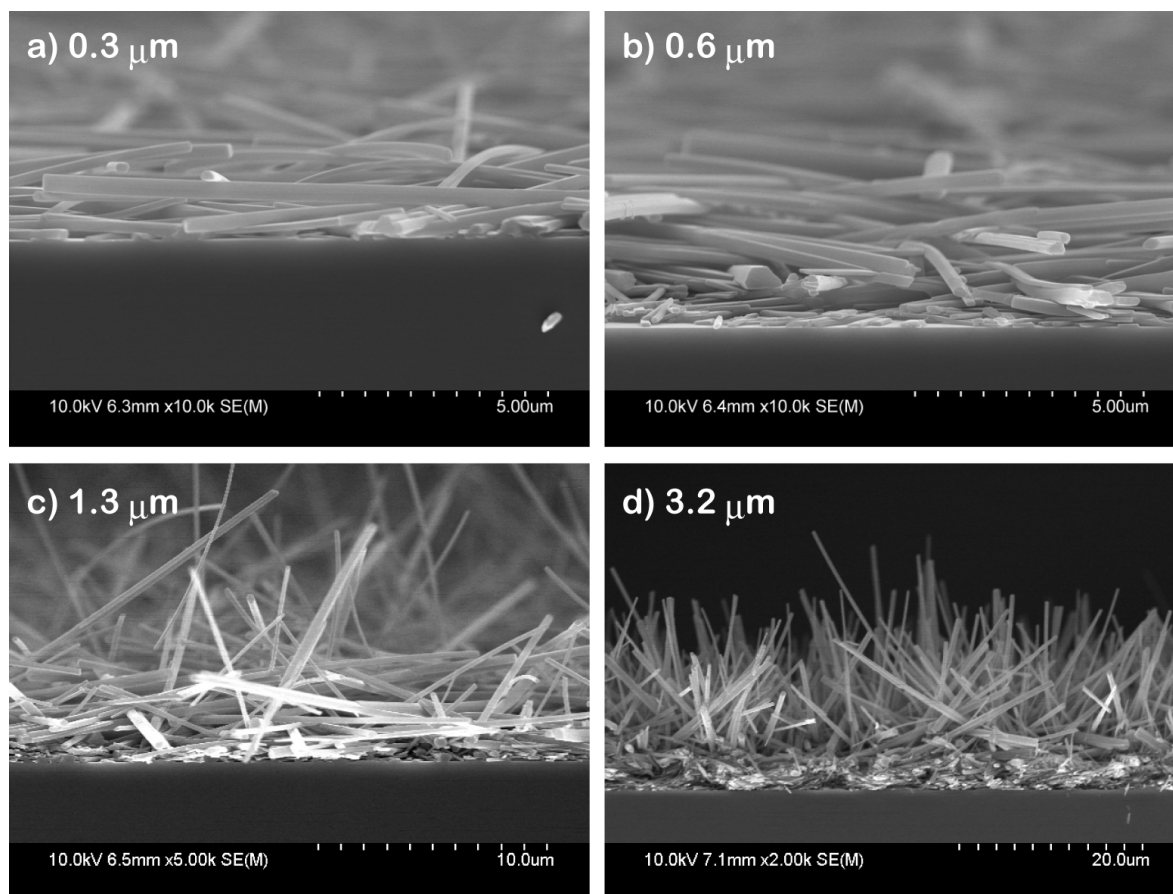
*Fabrication of superhydrophobic peptide film:* Amorphous thin peptide film was prepared by drying a drop of diphenylalanine solution in HFIP under an anhydrous condition in a glove box (model: MOGB 1S, Moisture Oxygen Technology Co., Korea), and then treated with pentafluoroaniline vapor (or aniline vapor for the control experiment) at 100 °C for 12 h. A self-cleaning superhydrophobic surface was prepared by treating as-synthesized superhydrophobic peptide nanowire film by rapidly cooling the growth chamber temperature from 100 °C to 50 °C to induce a slight wetting for the rearrangement of peptide nanowires into hierarchical nano/microstructures. The thickness of amorphous peptide thin film was controlled by varying the concentration of diphenylalanine in HFIP from 5 to 100 mg ml<sup>-1</sup>. To investigate the effect of aging temperature on the superhydrophobic characteristics of peptide thin films, we prepared the films at a constant temperature of 27, 50, 75, 100, 175, 250, and 300 °C.

*Characterization:* The morphology of peptide thin films before and after the solvent-vapor treatment was analyzed by an S-4800 field emission SEM (Hitachi Ltd., Japan). The static water contact angle of each surface was measured with a Phoenix 300 contact-angle meter (Surface Electro Optics Co., Ltd., Korea) at five different locations on each film using 6 mg of water droplet. The accuracy of contact

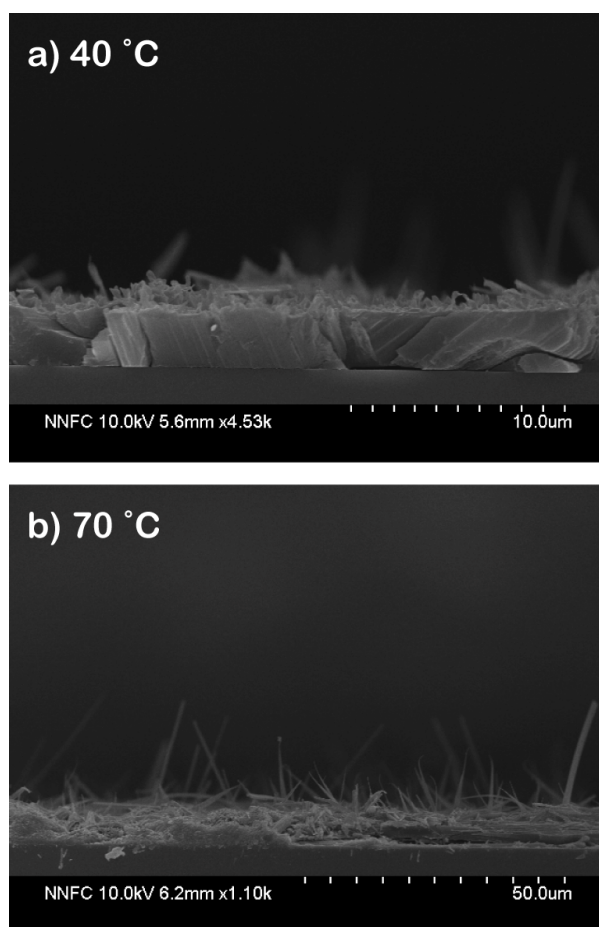
angle measurements is given with a standard deviation ( $n = 5$ ). The structure of thin peptide films was analyzed with a D/MAX-RC thin-film X-ray diffractometer (Rigaku Co., Japan) under the following conditions: scan range:  $2\text{--}60^\circ$ ; scan speed:  $3^\circ \text{ min}^{-1}$ ; Cu  $K\alpha$  radiation,  $\lambda=1.5418 \text{ \AA}$ . The incorporation of pentafluoroaniline into peptide nanowires during the self-assembly process was investigated by measuring their FT-IR and XPS spectra, using a Hyperion 3000 attenuated total reflection-Fourier transform infrared (ATR-FTIR) microscope (Bruker Optics Inc., Germany) and a JPS-9000MX spectrometer (JEOL Ltd., Japan), respectively.



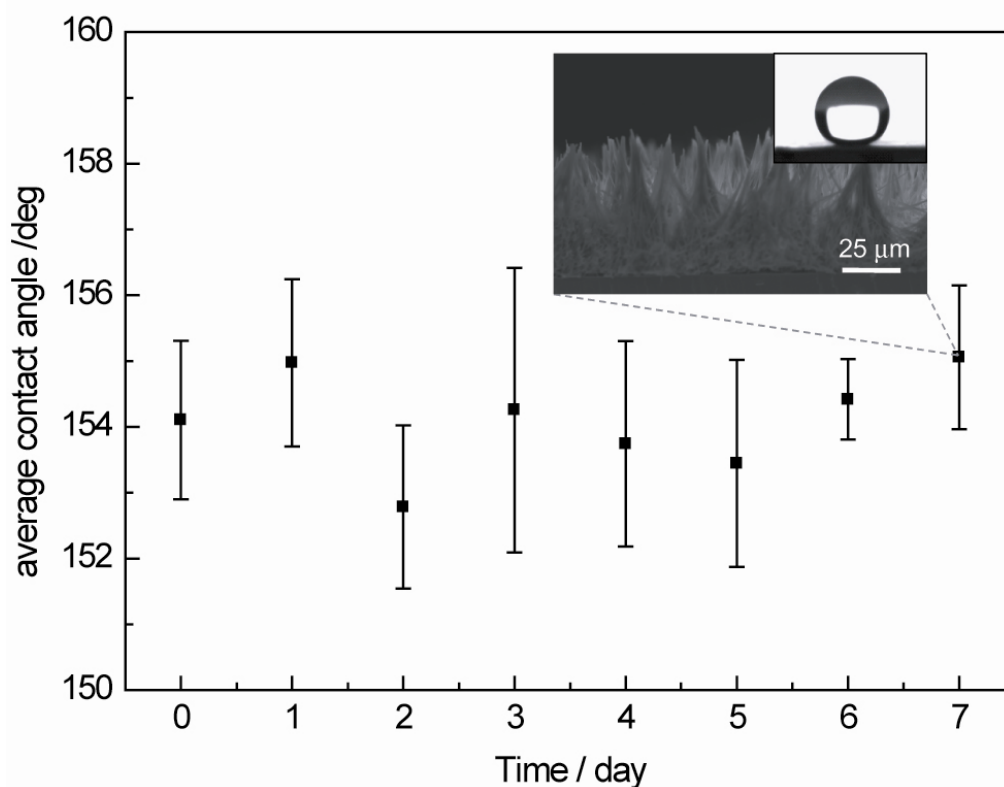
**Figure S1.** XPS spectra of diphenylalanine film before and after solvent-vapor (i.e., aniline or pentafluoroaniline) treatment at  $100^\circ \text{C}$ . Note that a trace amount of fluorine present in peptide nanowires even without pentafluoroaniline vapor treatment originated from residual HFIP molecules that were used when we prepared the amorphous peptide film.



**Figure S2.** Electron micrographs of peptide nanowires self-assembled from amorphous diphenylalanine films with four different thicknesses. The thickness of the amorphous peptide film was controlled by changing the concentration of diphenylalanine in HFIP. The final morphology of peptide nanowire film after the solvent-vapor treatment was highly dependent on the thickness of amorphous peptide thin film. When the amorphous peptide film was sufficiently thick ( $> 1 \mu\text{m}$ ), the solvent-vapor treatment led to the growth of vertical peptide nanowires by the surface-initiated nucleation and growth mechanism. However, peptide nanowires grew parallel to their substrate when the film thickness was not thick enough, implying that the free energy at the interface between the peptide film and the underlying substrate may affect the growth of peptide nanowires.



**Figure S3.** Electron micrographs of peptide films treated with pentafluoroaniline vapor at 40 °C and 70 °C for 12 h, respectively. At the temperatures lower than 100 °C, the self-assembly of diphenylalanines into nanowire structures was depressed and became very slow.



**Figure S4.** The stability of superhydrophobic peptide nanowire films. Between each measurement, peptide nanowire films were exposed to atmosphere. There was no significant change in their superhydrophobic characteristics even after a week of incubation. The inset shows the photograph of a water droplet on the peptide nanowire film and the electron micrograph of film morphology at 7<sup>th</sup> day.