Supplementary Information for

Controlled Three-Dimensional Structures for Liquid Repellency Engineering

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S1. Three-dimensional (3D) nanoshell structures of TiO_2 with interconnected capillary spaces

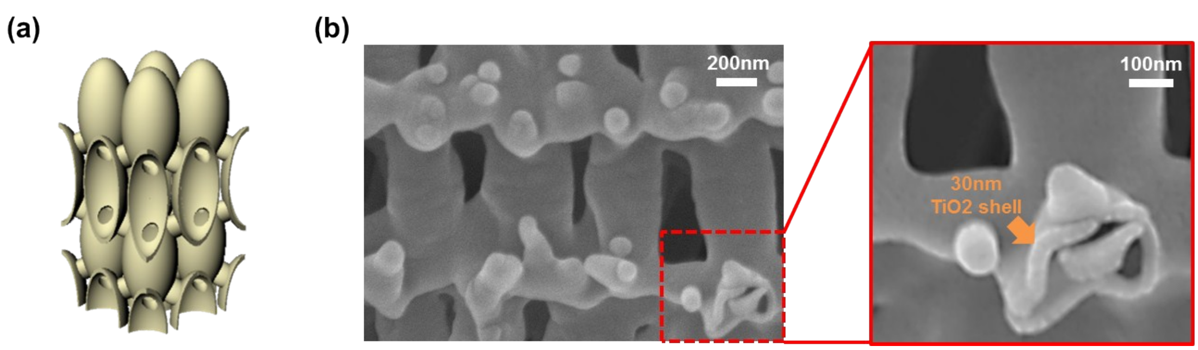

Fig. S1. (a) Schematic illustration of the 3D-nanoshell-structured-TiO_2 with multiple layers (2 >layers), (b) High-magnification FE-SEM images of the 3D-nanoshell-structured TiO_2.

S2. Transparency properties of 3D-nanoshell-structured TiO_2

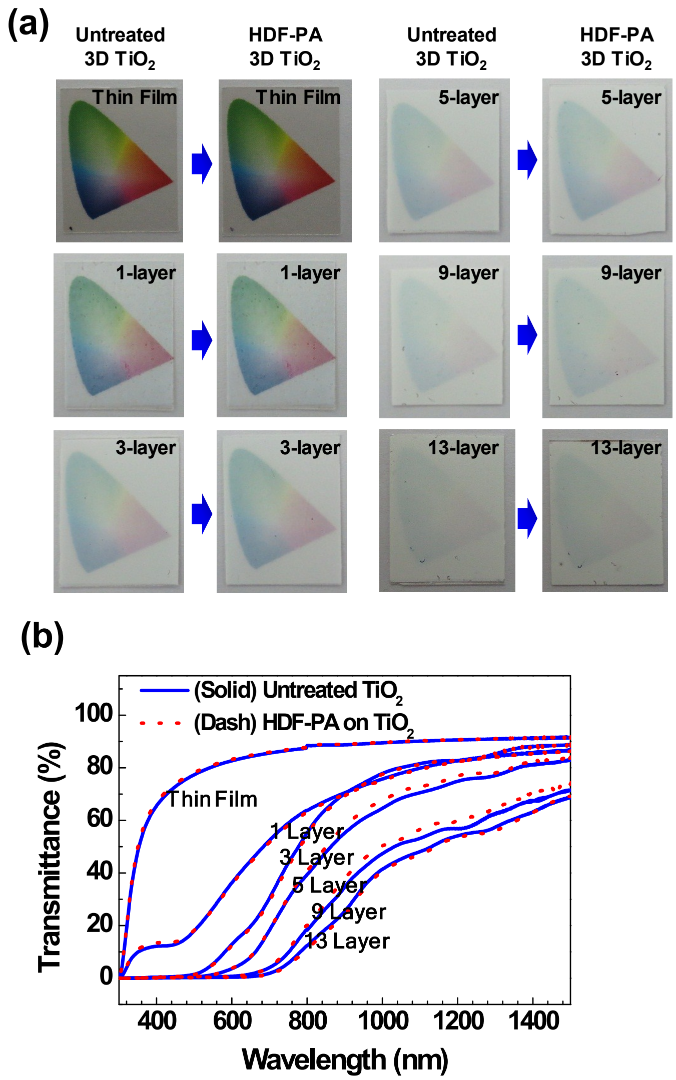

Fig. S2. Transparency properties of 3D-nanoshell-structured TiO_2 with periodic interconnected capillary spaces. (a) Optical images of a region of the substrates containing 50 × 50 mm^2 patterns. (b) Optical transmission spectra of regions of 25 × 25 mm^2. 3D-nanoshell-structured TiO_2 samples consisting of 1, 3, 4, 9, and 13 layers.

Figure S2(a) presents optical images of the 3D nanoshell structures of TiO_2 with six different thicknesses (flat, 1, 3, 5, 9, and 13 layers). The image of the Commission

Internationale de L'Eclairage (CIE) coordinates in the background was observed through 3D nanoshell structures of TiO_2. Figure S2(b) presents the transmittance values versus the number of layers both before and after HDF-PA treatment. According to these results, in the wavelength range of 350–1450 nm, the color coordinate image of the substrate background was visible to some extent even with increasing layers. The transmittance at a wavelength of 700 nm was 52.4% for 1 layer, 30.5% for 3 layers, 18.2% for 5 layers, 4.0% for 9 layers, and 1.9% for 13 layers before the HDF-PA treatment. After treatment, these values were 51.7%, 29.4%, 18.6%, 4.3%, and 1.5%, respectively. These data indicate a decreasing trend with an increasing number of layers. The transmittance (at 700 nm) of the unstructured TiO_2 thin film before and after HDF-PA addition was 85.6% and 86.0%, respectively. No significant change was observed in transmittance before and after the addition of the HDF-PA SAM. It is assumed that the TiO_2 surface was coated with monolayer perfluorocarbon to a thickness of several nanometers, and accordingly, the addition did not significantly affect the transmittance.

S3. Surface roughness of 3D-nanoshell-structured TiO_2 using atomic force microscopy (AFM)

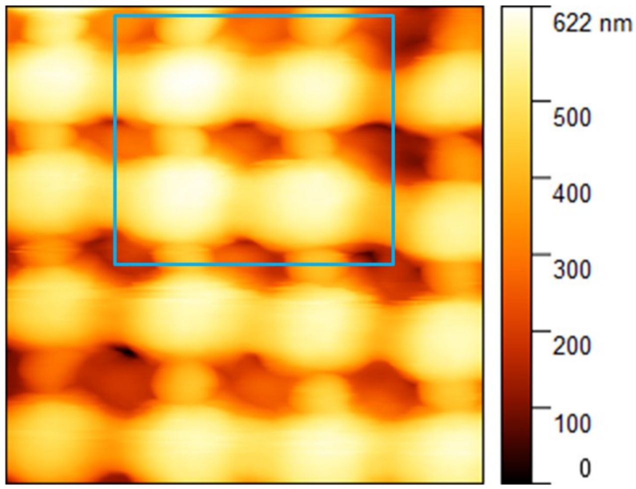

Fig. S3. The topographical image of 3D-nanoshell-structured TiO_2. (blue square: unit cell) Actual surface area = 2.25 μm^2, projected area = 1.177 μm^2.

We measured the surface roughness of 3D-nanoshell-structured TiO_2 using atomic force microscopy (AFM). We added the roughness data of 3D-nanoshell-structured TiO_2. The 3D-nanoshell-structured TiO_2 with 1, 3, 5, 9 and 13 layers showed the similar roughness of ~1.27.

S4. The average and standard deviation of the measured contact angle values (Figure 3)

Table S1. Contact angles of TiO_2 thin film and 3D-nanoshell-structured TiO_2 arrays with 1, 3, 5, 9, and 13 layers

	Number of layer					
	0	1	3	5	9	13
Contact Angle	101.0 ± 0.3°	123.4 ± 2.3°	134.9 ± 0.9°	141.8 ± 1.2°	148.5 ± 0.6°	151.3 ± 0.3°

Table S2. Contact angles of HDF-PA SAM-coated 3D-nanoshell-structured TiO_2 and the shapes of 6 different liquid droplets (DI water, dextrose, normal saline, amino acid injection, blood, and oil)

	Liquids					
	D.I. water	Dextrose	Saline	Amino acid	Blood	Oil
Contact Angle	148.9 ± 0.6°	146.7 ± 0.8°	144.5 ± 1.0°	137.2 ± 1.5°	121.8 ± 2.2°	115.0 ± 2.1°

S5. The contact angles of five solvents with well-known surface tension (*i.e.*, DMSO, chlorobenzene, toluene, acetone, and ethanol).

Table S3. Contact angles of HDF-PA SAM-coated 3D-nanoshell-structured TiO_2 of five different liquids (DMSO, chlorobenzene, toluene, acetone, and ethanol)

Liquid	**Contact angle**	**Surface tension ($mN{\cdot}m^{-1}$)**
Dimethyl sulfoxide (DMSO)	70.8 ± 2.6°	44.0
Chlorobenzene	69.4 ± 1.5°	33.6
Toluene	56.7 ± 2.5°	28.5
Acetone	44.1 ± 2.5°	23.7
Ethanol	34.6 ± 2.5°	21.4