Electronic Supplementary Material (ESI) for RSC Advances.

Material-independent Fabrication of Superhydrophobic Surfaces by Mussel-inspired Polydopamine

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Supporting information

Materials

Dopamine hydrochloride, titanium(IV) isopropoxide (99.999%, trace metals basis), potassium phosphate dibasic trihydrate, calcium chloride (≥93.0%), tris(hydroxymethyl)aminomethane, and 2-propanol (≥ 99.5%) were purchased from Sigma-Aldrich. Zonyl® FSE was purchased from Fluka. Sodium chloride was purchased from Duchefa Biochemies (Netherlands). Silicon (Si) substrates were purchased from Nanofab center (Korea). Gold (Au) and titanium (Ti) substrates were prepared by thermal evaporation onto the silicon wafers (thickness = 100 nm). Glass substrates were purchased from Paul Marienfeld GmbH & Co. KG (Germany). Aluminum (Al) was purchased from Alfa-Aesar (USA). Stainless steel, copper (Cu), Teflon, polypropylene (PP), polyethylene terephthalate (PET), polycarbonate (PC), and polyester were purchased from Kumjeong Inc. (Korea).

Polydopamine (pDA) coating

The pDA coating was performed by immersing bare surfaces in a dopamine hydrochloride solution (2 mg/mL, pH 8.5, 10 mM Tris buffer) for 16 h.[1]

The pDA/TiO_2/F functionalization

A titanium(IV) isopropoxide solution (~ 20 %) (the titanium isopropoxide solution (99.99 %) was five times diluted using 2-propanol) was poured onto the pDA-coated surface and immediately spin-coated at 1000 rpm for 15 sec, resulting in the immediate formation of TiO_2 on the surface (the spin-coating was carried out at room temperature and at relative humidity of 60%). The substrates were then immersed in an ethanol solution of 1% zonyl®FSE for 20 minutes to functionalize the surface with the perfluorophosphate surfactant.

Anti-icing test

Super-cooled water was prepared by storing DI water at -60 °C for 30 minutes prior to the anti-icing experiments. The pDA/TiO_2/F Al surface, bare/TiO_2/F Al surface, and bare Al

surface were similarly stored at -60 °C for 30 minutes before the experiment. As the super-cooled water was poured onto each surface, the formation of ice was time-dependently observed by a digital camera.[2]

Preparation of the supersaturated calcium phosphate solution (1.5X CaP solution)

Sodium chloride (6.224 g) and the potassium phosphate (0.257 g) were dissolved in 500 mL of DI water. The pH of the solution was then brought to 2~3 by the addition of a hydrochloride solution (1 M). Calcium chloride (0.312 g) was then dissolved in the solution, and the solution pH brought to 7.4 by the addition of 1 M Tris(hydroxymethyl)aminomethane.

The pDA/CaP/F functionalization

The pDA-coated substrates were immersed in a 1.5X CaP solution for 10 seconds and withdrawn without residual solution removal. The samples were placed on a slide glass and left to dry for 10 minutes at room temperature, followed by immersion of the substrates in DI water for 1 minute. This process was repeated eight times. Then, the treated substrates were immersed in the 1.5X CaP solution for 24 h at 37 °C. To modify the pDA/CaP surfaces with the zonyl®FSE, the resulting surfaces were immersed in an ethanol solution of 1% zonyl®FSE for 20 minutes.[3-4]

Characterization

Static contact angles were measured with a Phoenix 300 goniometer (Surface Electro Optics Co., Ltd., Korea). Static water contact angles were measured at three different locations on each sample, and the average values are reported. The advancing and receding contact angles were measured with a contact angle-meter (SEO Phoenix 300, Korea). Water droplets (5 μL) were placed on the substrates and the angle of the stage was slowly increased (0.5 deg./sec.) until the droplet started to roll. TiO_2 coating was monitored by field emission SEM (S-4800, Hitachi). XPS was performed with an ESCA 2000 (Thermo VG Scientific, England) with a

monochromatic twin X-ray source (Mg/Al target). Emitted photoelectrons were detected with a multichannel detector at a takeoff angle of 45° relative to the surface. During the measurements, ultralow vacuum (10^{-9} to 10^{-10} Torr) in the analysis chamber was maintained. The thickness of the adsorbed serum protein was measured with a Gaertner L116s ellipsometer (Gaertner Scientific Corporation, IL) equipped with a He-Ne laser (632.8 nm) at a 70° angle of incidence. A refractive index of 1.46 was used for all samples.

Results and Discussion

Schematic explanation of the methods for general preparation of superhydrophobic surfaces on any type of material surface using pDA

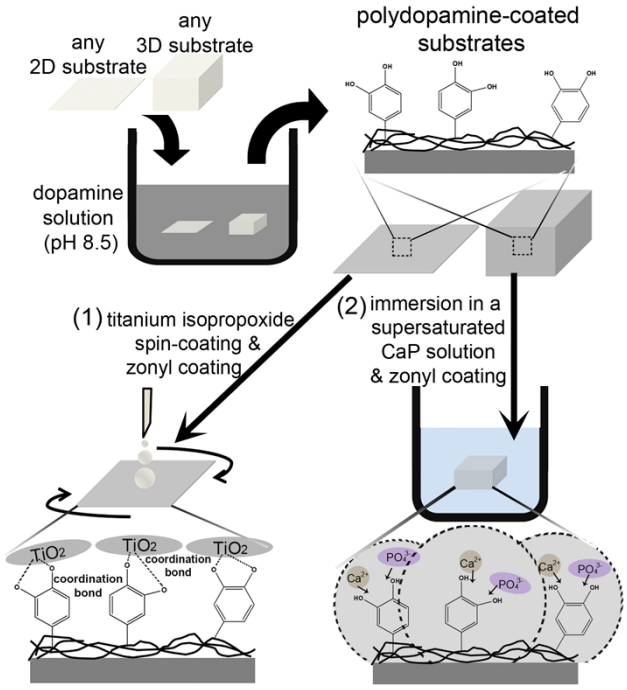

Figure S1. Schematic explanation of fabrication methods of superhydrophobic surfaces using the pDA-coated substrates. Two methods are used: (1) pDA/TiO_2/F (left); (2) pDA/CaP/F (right).

The fabrication of the pDA-TiO2 substrates: XPS study.

After the TiO_2 formation on the pDA, the appearance of a Ti2p peak and disappearance of the N1s peak indicated the successful formation of TiO_2 on the pDA. After the immersion of the pDA/TiO_2 surface in the ethanol solution of 1% zonyl®FSE, the appearance of F1s peak confirmed the successful modification with the perfluorophosphate surfactant.

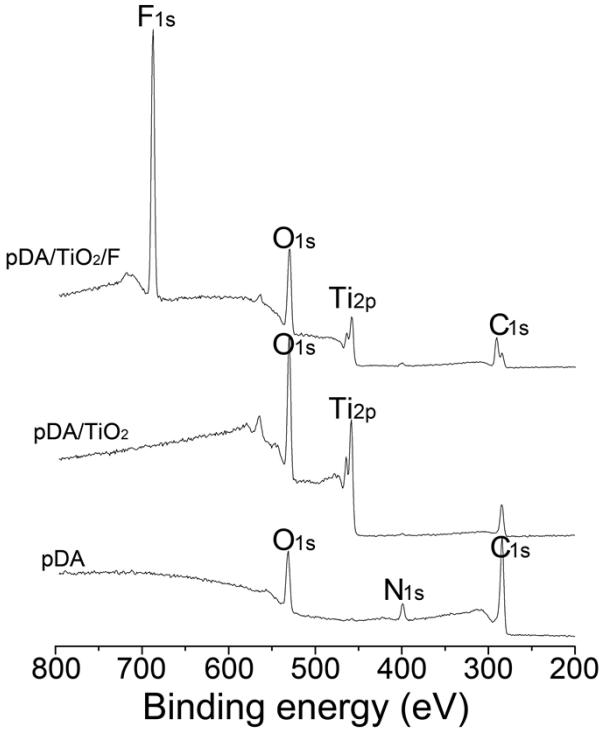

Figure S2. Survey scanned XPS spectra after pDA coating (bottom), TiO_2 formation (middle), and zonyl®FSE deposition (top)

The fabrication of the pDA-CaP substrates: XPS study.

The appearance of a P2p peak confirmed the successful formation of the CaP on the pDA. After the immersion of the pDA/CaP surface in the ethanol solution of 1% zonyl, the appearance of a F1s peak confirmed the successful modification with perfluorophosphate surfactant.

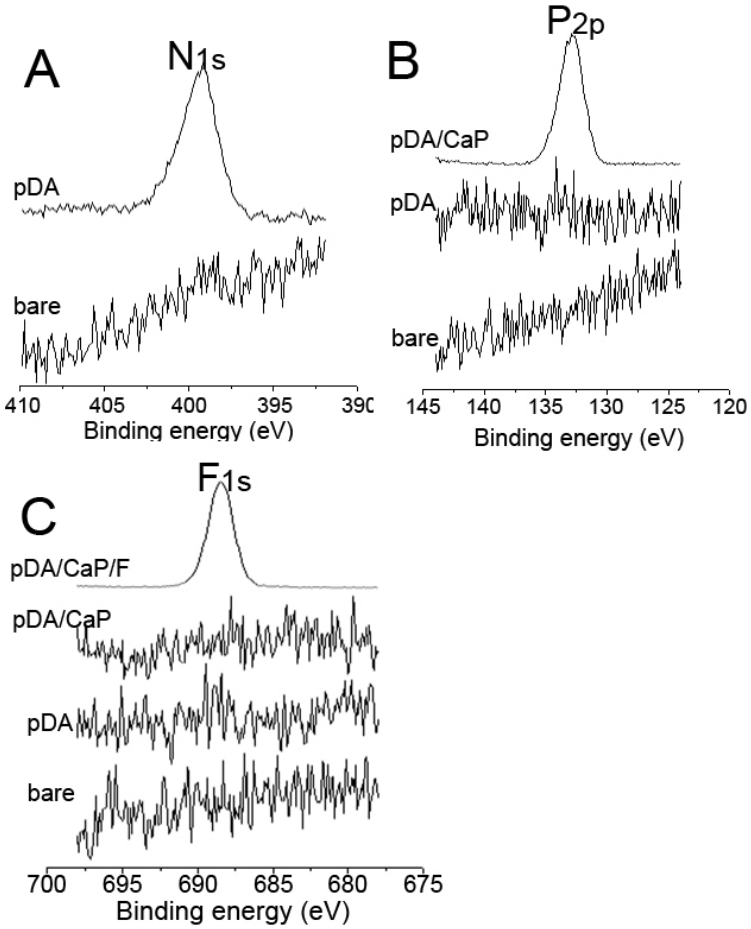

Figure S3. (A) High-resolution N1s XPS spectra of the bare Si surface and pDA-coated Si surface. (B) High resolution P2p XPS spectra of the bare Si surface, pDA-coated Si surface, and pDA/CaP Si surface. (C) High-resolution F1s XPS spectra of the bare Si surface, pDA-coated Si surface, pDA/CaP Si surface, and pDA/CaP/F Si surface.

Thickness of the TiO_2 and CaP layer

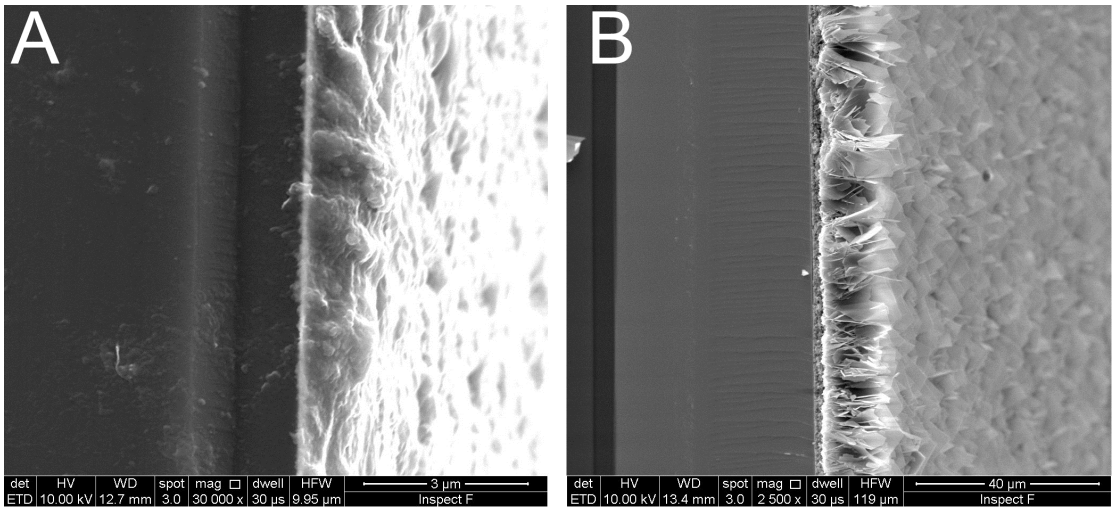

Figure S4. SEM cross-section images of (A) the pDA/TiO_2/F Si surface and (B) pDA/CaP/F Si surface.

Uniform dispersity of the micro-/nano-structured TiO_2 coating

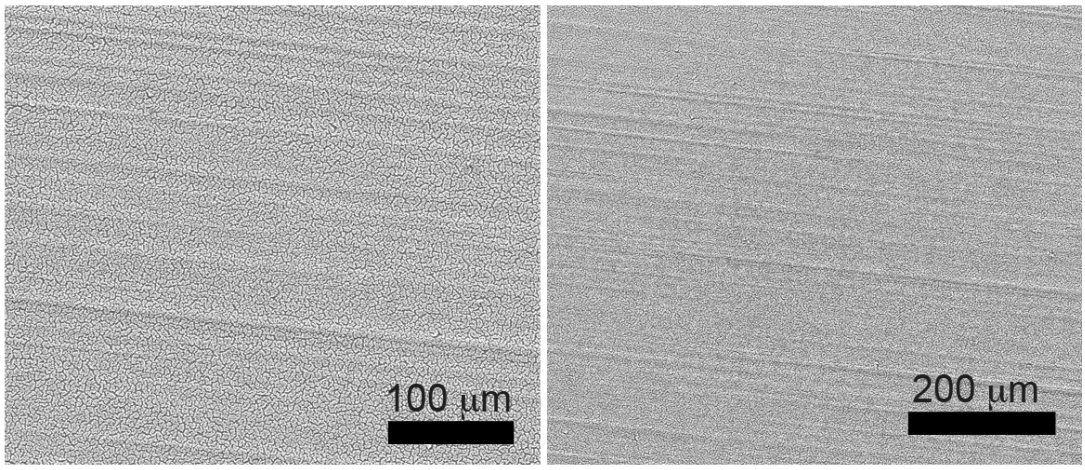

Figure S5. Low-resolution SEM images of the micro-/nano-structured TiO_2.

Dynamic contact angle analysis and anti-icing test of the pDA/TiO_2/F surface

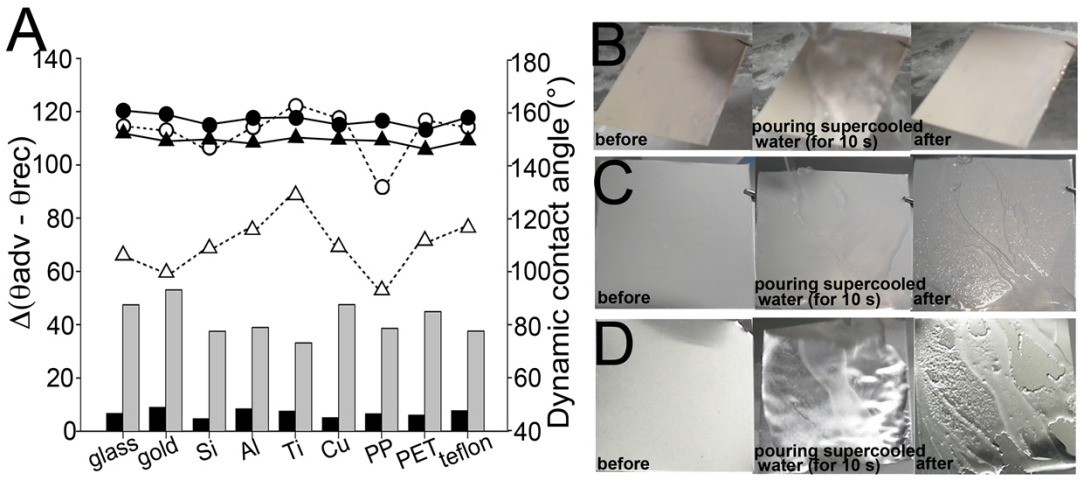

Figure S6. (A) Dynamic contact angle analysis (θadv: advancing, θrec: receding). The left Y-axis corresponds to the bar results, and the right Y-axis corresponds to the dynamic contact angles. θadv for pDA/TiO_2/F (close circle), θrec (close triangle), θadv for no-pDA/TiO_2/F (open circle), and θrec (open triangle). The bar graphs show contact angle differences (i.e., θadv – θrec) for pDA/TiO_2/F (black) and for no-pDA/TiO_2/F (gray). (B-D) Supercooled water (-60 °C) was poured onto the supercooled pDA/TiO_2/F (B), no-pDA/TiO_2/F (C), and unmodified Al surfaces (D).

Water static CA images of the pDA/CaP/F surfaces

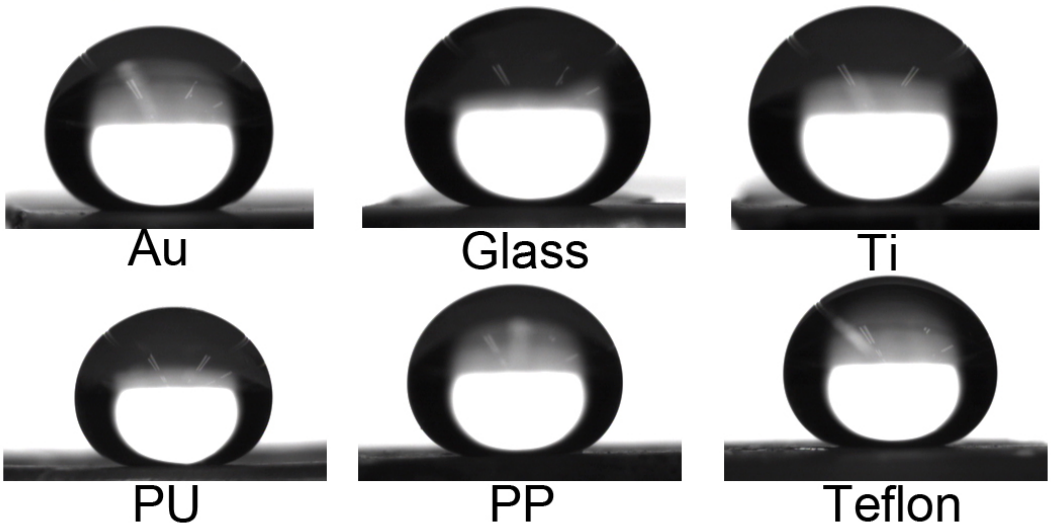

Figure S7. Water CA images of the pDA/CaP/F surfaces.

References

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[2] L. Cao, A. K. Jones, V. K. Sikka, J. Wu and D. Gao, *Langmuir*, 2009, **25**, 12444.
[3] J. Ryu, S. H. Ku, H. Lee and C. B. Park, *Adv. Funct. Mater.*, 2010, **20**, 2132.
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