Supplementary Material (ESI) for Chemical Communications
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Smart Surface of Water-induced Superhydrophobicity

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Electronic Supplementary Information

Experimental Details:

Materials: *N*-isopropylacrylamide (NIPAAm, 97%, Aldrich) was purified by recrystalization in hexane for three times. Acryloyl chloride (96%, Aldrich) and bromoisobutyryl bromide (97%, Alfa Aesar) was stored in refrigerator. *S*-Benzyl-L-cysteine (97%, Aldrich), D-aspartic acid (99%, Aldrich), *o*-phthaldialdehyde (OPA, 98%, Alfa Aesar), 3-aminopropyl-trimethoxysilane (ATMS, 97%, Fluka), Cu(I)Br (99.99%, Aldrich), pentamethyl diethylene triamine (PMDETA, 99 %, Aldrich), polyphosphoric acid (PPA), and other general solvents were used as received. Toluene and dichloromethane were dried sufficiently by molecular sieves. The methanol/alkali solutions were prepared by dropping 60 μL 2 N NaOH in 5.0 mL methanol and were used freshly. Deionized water (18.2 MΩcm, MilliQ system) was used.

Synthesis and Characterization of N-acryloyl-S-benzyl-L-cysteine monomer: *S*-benzyl-L-cysteine (2.11 g, 10 mmol) were dissolved in 10 mL 1 N NaOH, and with stirring at 0 °C, acryloyl chloride (1.36 g, 15 mmol) were added dropwise within 30 min. The pH of the reaction mixture was held by addition of 2 N NaOH at about 11.0 by use of pH-stat at the beginning of the reaction and was allowed to decrease to neutrality within 1 hour. Then the reaction was moved to room temperature. After 1 hour the solutions were acidified to pH 2.0 by addition of 2 N HCl, and the monomer were extracted with ethyl acetate (4 × 30 mL) and the organic phase was dried with anhydrous sodium sulphate and evaporated to dryness. The oily residues were characterized by HRMS (Fig. S1, MS-MALDI, m/z): $[M + H]^+$: 266.0842, and $[M + Na]^+$: 288.0661; and ^{1}H NMR (Fig. S2, 300 MHz, DMSO-d_6, δ): 12.77 (s, 1H; COOH), 8.5 (d, J = 9 Hz, 1H; NH), 7.2 ~ 7.3 (m, 5H; Ar H), 6.3 (d, J = 18 Hz, 1H; C=CH), 6.1 (d, J = 15 Hz, 1H; $CH_{2(a)}$=C), 5.6 (d, J = 9 Hz, 1H; $CH_{2(b)}$=C), 4.5 (t, J = 9 Hz, 1H; CH), 3.78 (s, 2H; Bn CH_2), 2.8 (d, J = 12 Hz, 1H;

$CH_{2(a)}$–S), 2.6 (d, J = 12 Hz, 1H; $CH_{2(b)}$–S); trace of ethyl acetate was found (δ): 4.0 (d, J = 9 Hz, 2H; CH_2), 1.9 (s, 3H; CH_3–C=O), 1.1 (t, J = 6 Hz, 3H; CH_3).

Preparation of the structured substrate: The structured Si substrate with patterned pillars array (Fig. S3 a and b) was obtained by lithography etching. The dimensions of the pillars in our experiment were 10 μm × 10 μm, and the height was 20 μm. The nanostructures on the chapiter (Fig. S3 c and d) were further formed by an aqueous electroless etching (EE) method. The patterned Si substrates were carefully put in a solution of hydrofluoric acid with silver nitrate, at 50 °C for about 3 min, and the nanostructures were obtained on the pillars.

Synthesis of P(NIPAAm-co-Cy) thin films on silicon substrates – "grafting from" process: A clean silicon substrate was firstly treated to generate surface hydroxy groups. After dried under a nitrogen flow, it was immersed and heated to reflux in toluene with 5 wt.-% ATMS for 3 h to obtain surface $–NH_2$ groups. Then it was rinsed with toluene and dichloromethane, dried, and immersed in dichloromethane with pyridine (2% v/v). Bromoisobutyryl bromide was added dropwise into above solution at 0 °C, and the mixture was left for 1 h at this temperature, and then at room temperature for 12 h. The substrate was cleaned with dichloromethane and toluene. Polymerization of P(NIPAAm-*co*-Cy) was achieved by immersing the dried substrate in a degassed solution of NIPAAm (0.91 g) and *N*-acryloyl-*S*-benzyl-L-cysteine monomer (0.24 g, 10 mol-% against to the total molar fraction) in a 1:1 (v/v) mixture of H_2O and MeOH (10 mL) containing Cu(I)Br (0.032 g) and PMDETA (0.14 mL) for 2.5 h at 60 °C. Under these conditions, the film thickness was about 60 nm.

Derivatization procedure – "grafting to" process: To 0.30 g PPA in 20 mL xylene, the silicon substrates modified with P(NIPAAm-*co*-Cy) films were immersed and refluxed under nitrogen gas atmosphere. After 3 h, the solution was cooled firstly, and then the substrates were washed with methanol and subsequently immersed in 10 mL OPA solution (0.025 g OPA in 10 mL methanol). For derivatization, the solution of aspartic acid (0.020 g in 1.0 mL NaOH solution) was added to the mixed OPA solution. After 30 min, the silicon substrates were washed with methanol to remove any residues, and then dried under a nitrogen flow.

Instruments and Characterization: Field-emission scanning electron microscope (JSM–6700F, Japan) was used to obtain SEM images of the substrates. Water contact angles (CAs) were measured on an OCA20 machine (DataPhysics, Germany) at appointed temperature with saturated humidity. Deionized water droplets (about 1 μL) were dropped carefully onto the surface. An average CA value was obtained by measuring the same sample at four different positions.

Spectra:

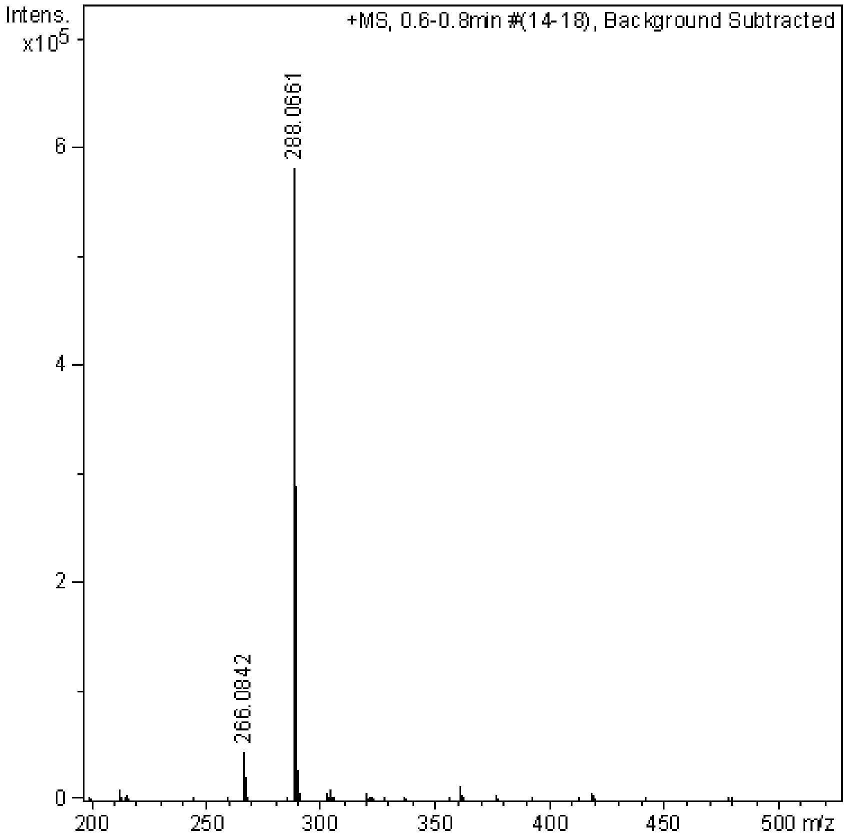

Fig. S1 MS-MALDI spectra of *N*-acryloyl-*S*-benzyl-L-cysteine monomer.

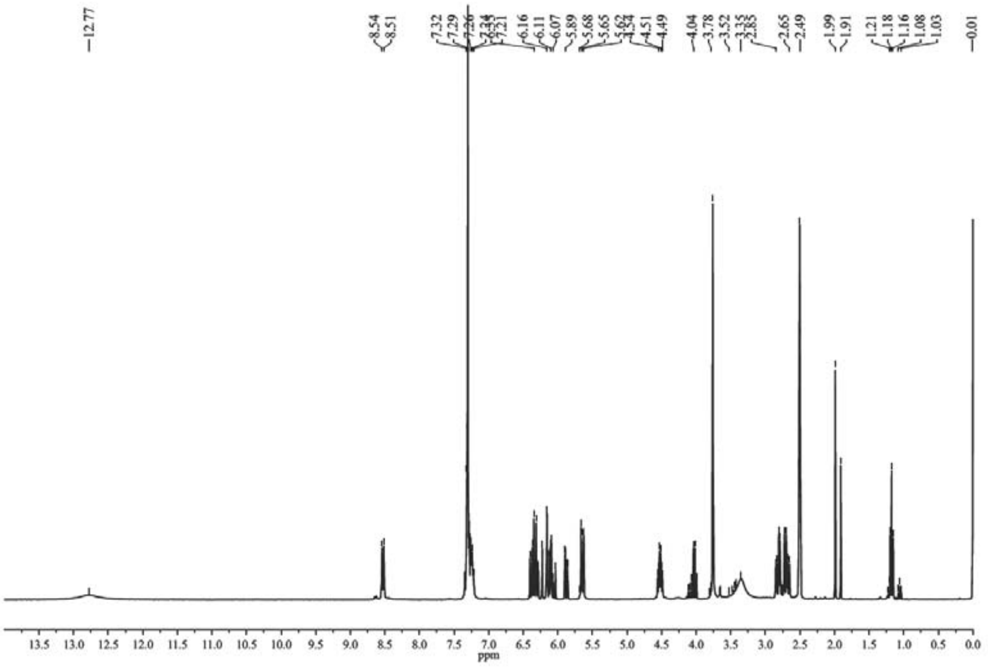

Fig. S2 ^{1}H NMR spectra of *N*-acryloyl-*S*-benzyl-L-cysteine monomer.

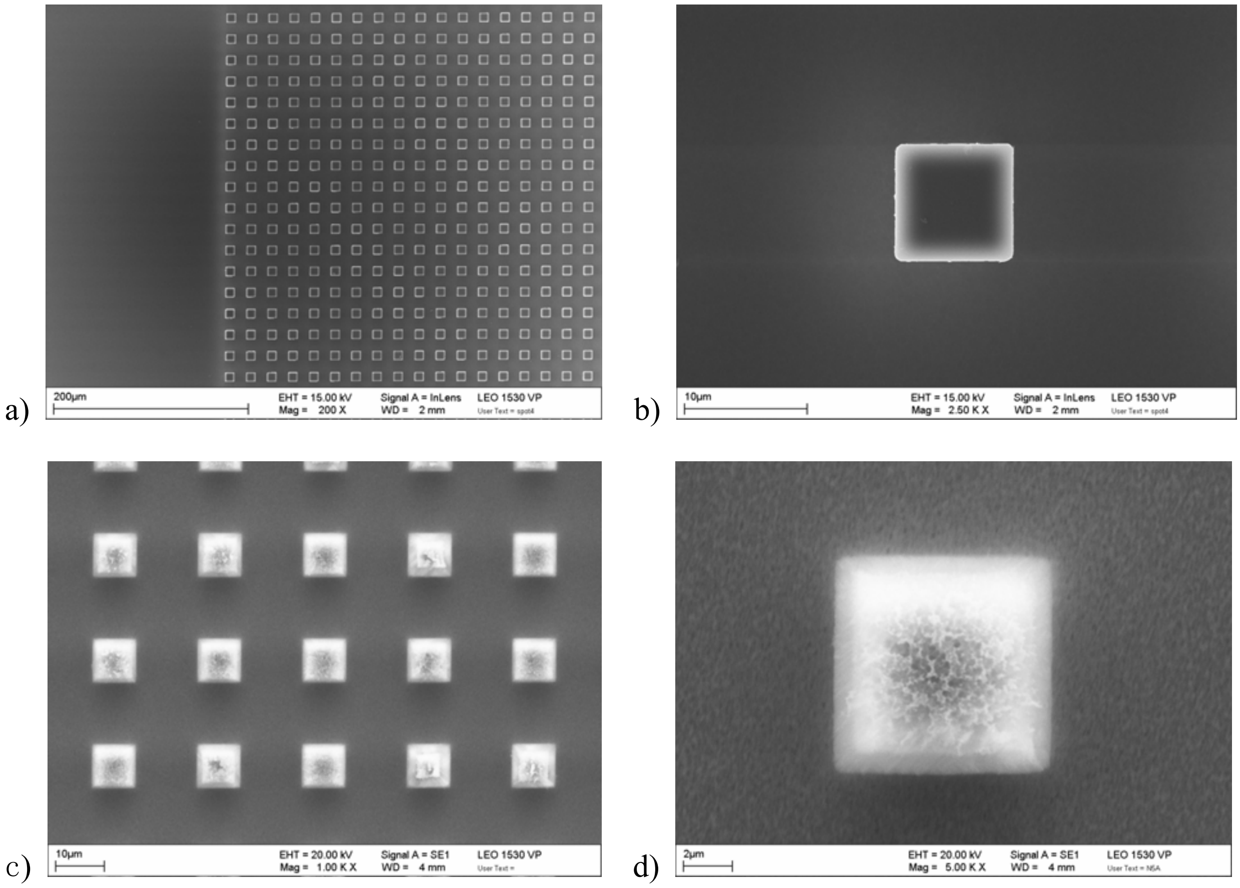

Fig. S3 SEM images of the structured Si substrates: (a) the raw pillar array at low magnification and (b) high magnification for a single pillar with smooth chapiter; (c) the etched pillars array at low magnification and (d) high magnification for a single pillar with nano-structures.