Surface Chemistry

Reversible Switching between Superhydrophilicity and Superhydrophobicity**

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Wettability is a very important property that is governed by both chemical composition and surface structure.[1–9] Recently, the control of surface wettability has aroused great interest because of its wide variety of applications. In general, superhydrophobic surfaces[1–6] with a water contact angle (CA) greater than 150° can be obtained by controlling the topography of hydrophobic surfaces, while superhydrophilic surfaces with a CA about 0° can be realized through a 3D[7–8] or 2D capillary effect[9] on hydrophilic surfaces. Stimuli-responsive surfaces[10] make it possible to reversibly control the wettability of the surface and has been demonstrated by various methods, including light-irradiation,[11,12] use of an electric field,[13,14] thermal treatment[15] and treatment with solvent.[16] However, reversible switching between superhydrophilicity and superhydrophobicity has never been reported. Herein we show the roughness-enhanced thermally responsive wettability of a poly(*N*-isopropylacrylamide) (PNIPAAm)-modified surface.[17,18] Reversible switching between superhydrophilicity and superhydrophobicity can be achieved in a narrow temperature range of about 10 °C, which is considered to result from the combined effect of the chemical variation of the surface, and surface roughness. Such switchable surfaces may have wide applications in functional textiles, intelligent microfluidic switching, controllable drug release, and thermally responsive filters.

Surface-initiated atom-transfer radical polymerization[19,20] was used to fabricate thermally responsive PNIPAAm thin films[21–24] on both a flat and a rough silicon substrate. Results from atomic force microscopy (AFM) and scanning electron microscopy (SEM) showed that the thickness of the PNIPAAm thin film could be well controlled by the polymerization time. Figure 1 a (left) shows a typical SEM image of a rough substrate that has been modified with a PNIPAAm thin film. Compared with the smooth surface (Figure 1 a right) of the flat substrate, the rough substrate exhibits a regular array of square silicon microconvexes (bright squares). The dark lines are microgrooves that are about 6 μm in width and about 5 μm in depth. These microgrooves were generated by a laser cutter (see Experimental Section) on a silicon wafer in a region of about 1 × 1 cm^2. The surface roughness can be adjusted by controlling the spacing between the grooves. In our experiments, different groove spacings of about 31 μm, 18 μm, 8 μm, and 6 μm were selected. The magnified image of the rough surface shows that both microconvexes and microgrooves were also rather rough (Figure 1 b). Further magnified SEM images of the silicon microconvexes before (Figure 1 c) and after (Figure 1 d) PNIPAAm polymerization show that these

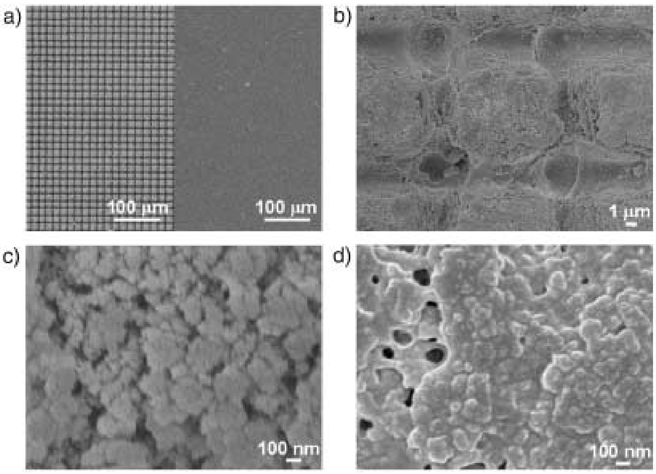

Figure 1. Typical SEM images of a rough substrate with groove spacing of about 8 μm. For all substrates, the width and depth of microgrooves were controlled to about 6 μm and about 5 μm, respectively. The spacing between microgrooves could be varied, thus adjusting the surface roughness of the substrates. Four groove spacings of about 31 μm, 18 μm, 8 μm and 6 μm were selected. a) SEM image for the regular array of silicon microconvexes with PNIPAAm modification (left), compared with that of flat substrate (right). b) Magnified image of the microconvex array in the right of (a). c) Nanostructures on a single microconvex without PNIPAAm modification. d) Nanostructures on a single microconvex with PNIPAAm modification.

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surfaces are composed of many irregular nanoparticles and pores. The nanoparticles were sputtered from adjacent microgrooves and the pores were formed by the aggregation of nanoparticles. Although the nanoporous structure of the surface was partially filled by PNIPAAm polymerization, the micro- and nanostructures of the substrates remained after polymerization.

For the flat substrate, PNIPAAm thin film exhibited thermally responsive switching between hydrophilicity and hydrophobicity. When the temperature changed from 25 °C to 40 °C, the water CA increased from 63.5 ± 2.6° to 93.2 ± 2° (Figure 2 a). This effect is explained by the competition between intermolecular and intramolecular hydrogen bonding below and above the lower critical solution temperature (LCST) of about 32–33 °C (Figure 2 b).[25] At temperatures below the LCST, the predominantly intermolecular hydrogen bonding between the PNIPAAm chains and water molecules contributes to the hydrophilicity of PNIPAAm film. At temperatures above the LCST, intramolecular hydrogen bonding between C=O and N−H groups in the PNIPAAm chains results in a compact and collapsed conformation of PNIPAAm chains, which makes it difficult for the hydrophilic C=O and N−H groups to interact with water molecules. Thus, the film exhibits hydrophobicity at high temperatures.

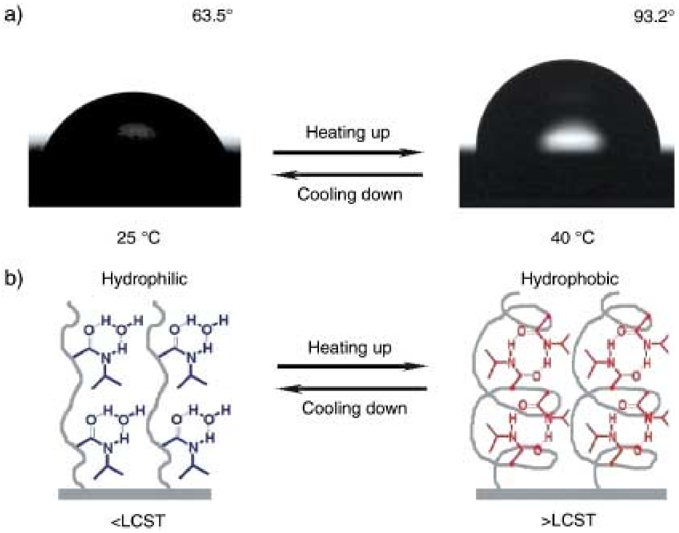

Figure 2. Thermally responsive wettability for a flat PNIPAAm-modified surface. a) Change of water drop profile when temperature was elevated from 25 °C (left) to 40 °C (right) with water CAs of 63.5 ± 2.6° and 93.2 ± 2°, respectively. b) Diagram of reversible formation of intermolecular hydrogen bonding between PNIPAAm chains and water molecules (left) and intramolecular hydrogen bonding between C=O and N-H groups in PNIPAAm chains (right) below and above the LCST, which is considered to be the molecular mechanism of the thermally responsive wettability of a PNIPAAm thin film.

As for the rough substrates with PNIPAAm modification, temperature-dependent experiments indicated that the thermally responsive wettability was greatly enhanced by surface roughness. This is in contrast to the substrates without PNIPAAm grafting, all of which showed superhydrophilicity, with a water CA of about 0°, and were temperature independent. Figure 3 a show the relationships between the water CA and the groove spacing, D, at 25 °C and 40 °C for the PNIPAAm-modified substrates. The water CA at 25 °C decreased from 63.5 ± 2.6° for a flat substrate (as denoted by groove spacing of ∞) to 33.5 ± 1.4° ($D = 31$ µm), 10 ± 0.6° (18 µm), ≈ 0° (8 and 6 µm). At 40 °C, the water CAs increased from 93.2 ± 2° (flat substrate) to 112.9 ± 2.6° ($D = 31$ µm), 128.9 ± 1.4° (18 µm), 137.9 ± 2° (8 µm), and 149.3 ± 2.5° (6 µm). These results indicate that thermally responsive switching between superhydrophilicity and superhydropobicity can be realized when the groove spacing of the substrate is small (ca. 6 µm), in other words, when the substrate is sufficiently rough. Figure 3 b shows photographs of water drop profile at 25 °C and 40 °C, respectively. The temperature dependences of water CA for the $D \approx 6$ µm rough substrate and the flat substrate was studied in detail and shown in Figure 3 c. The superhydrophobic/superhydrophilic switching temperature for flat and rough substrates were almost identical and lay around the LCST, thus indicating that the chemical property of the PNIPAAm thin film did not change with the variation of substrate structure. For the rough substrate, the surface exhibited a water CA of about 0° below 29 °C, whereas it was about 150° above 40 °C, thus indicating a thermally responsive switching between superhydrophilicity and superhydropobicity. We repeatedly cycled the temperature from 20 to 50 °C and recorded the variation of the water CA. The measurements of water CA at high and low

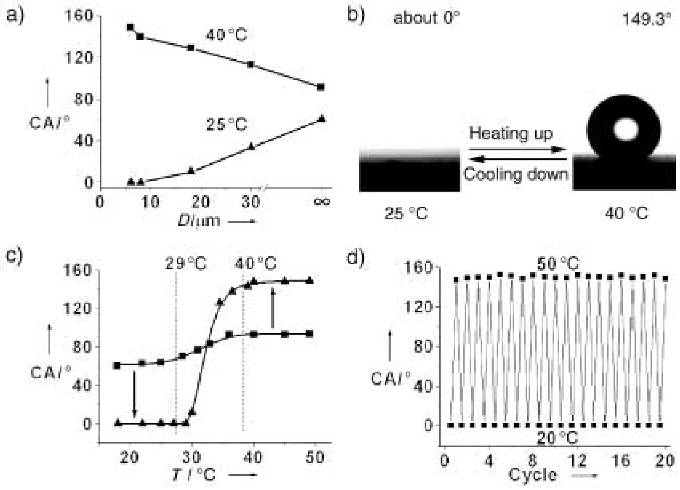

Figure 3. Surface-roughness-enhanced wettability of a PNIPAAm-modified surface. a) The relationships between groove spacing (D) of rough surfaces and the water CAs at low temperature (triangles, 25 °C) and at high temperature (squares, 40 °C). The groove spacing of ∞ represents flat substrate. b) Water drop profile for thermally responsive switching between superhydrophilicity and superhydrophobicity of a PNIPAAm-modified rough surface with groove spacing of about 6 µm, at 25 °C and 40 °C. The water CAs are about 0° and 149.3 ± 2.5°, respectively. c) Temperature (T) dependences of water CAs for PNIPAAm thin films on a rough substrate with groove spacing of about 6 µm (triangles) and on flat substrate (squares). d) Water CA in at two different temperatures for a PNIPAAm-modified rough substrate with groove spacing of 6 µm. Half cycles: 20 °C; and integral cycles: 50 °C.

temperatures were conducted on two sample stages, one set at 50 °C, the other at 20 °C. The results show excellent reversibility for more than 20 cycles (Figure 3 d) and a quick transformation between superhydrophilicity and superhydrophobicity as a single cycle lasts only several minutes. This reversibility remained after the samples had been laid aside without special protection for at least three months, which shows that the polymer film is stable. These results suggest that the thermally responsive switching between superhydrophilicity and superhydrophobicity is related to the combination of surface chemical composition and surface roughness. The former provides the thermally responsive chemical change of the surface between hydrophilicity and hydrophobicity, and the latter enhances these properties. Hydrophilicity at low temperatures is increased by surface roughness,[26] which also traps air when it comes into contact with water,[2–4,27] and enhances the hydrophobicity at high temperatures.

At low temperatures, the loosely coiled conformation of PNIPAAm chains and intermolecular hydrogen bonding with water molecules leads to high surface free energy and a small water CA. The film is hydrophilic and water enters the microgrooves beneath the water drop.[7,16] In this situation, surface roughness becomes the dominant factor intensifying the hydrophilicity. The microgroove structure, and the nanostructures on the microconvexes and microgrooves contributes to surface roughness, therefore the increasing hydrophilicity with the decrease of groove spacing can be explained by Wenzel's equation,[26] which describes the amplification effect of surface roughness on wettability. If the water CA on a flat surface is smaller than a critical CA on the rough surface, the imbibition of water will occur on the rough surface as a result of the 3D capillary effect.[7] The critical CA increases with an increase in surface roughness. For the substrates with a groove spacing of about 6 μm, the critical CA is in the range of 71–75° as calculated from surface roughness obtained by AFM measurements. The water CAs for flat PNIPAAm film below 29 °C are all close to or smaller than 71°. According to this study, the surface can exhibit superhydrophilicity below 29 °C (see Supporting Information). At higher temperatures, the compact and collapsed conformation of PNIPAAm chains induced by intramolecular hydrogen bonding between C=O and N−H groups in PNIPAAm chains leads to low surface free energy and large water CAs. The film is hydrophobic and the rough surface traps air. It was reported that the hydrophobicity of a rough surface can be intensified by increasing the air/water interface,[2–4,27] for example, superhydrophobic surfaces with water CAs larger than 170° have been obtained with aligned-nanotube[3] and -nanofiber[4] structures. For the rough surfaces in this study, only the upper part of the microconvexes can make contact with water molecules and thus the size of the air/water interface is controlled by the groove spacing. Therefore water CAs at high temperatures increase with a decrease in groove spacing. The nanostructures on the surfaces of microgrooves and microconvexes also contribute to the increase in the air/water interface and thus further enhance the hydrophobicity of PNIPAAm thin films on rough substrates at high temperatures.

In conclusion, the combination of the change in surface chemistry and surface roughness can enhance stimuli-responsive wettability. Reversible switching between superhydrophilicity and superhydrophobicity, which is a challenging thesis in surface chemistry, can be intelligently controlled through external stimuli. This method can be extended to other stimuli-responsive surfaces. This ability to control the wettability by changing the temperature has applications in a broad range of fields. For example, thermally responsive textiles, controllable drug release,[28] temperature-controlled microfluidic switches,[29] and thermally responsive filters for oil/water separation (see also Supporting Information).

Experimental Section

Synthesis of PNIPAAm thin films on silicon substrates: A clean silicon substrate was immersed in an aqueous NaOH solution (0.1 M) for 2 minutes and subsequently in HNO_3 (0.1 M) for 10 minutes to generate surface hydroxyl groups. After the substrate had been washed with an excess of water and dried under a flow of nitrogen, it was heated to reflux in toluene that contained 5 wt % aminopropyl trimethoxysilane (ATMS) for at least 6 h to obtain chemically bonded -NH_2 groups on the surface. The surface was rinsed with toluene and dichloromethane to remove remaining ATMS, dried under a flow of nitrogen gas, and immersed in dry dichloromethane that contained pyridine (2 % w/v). The polymerization initiator bromoisobutyryl bromide was added dropwise into the solvent containing the silicon substrate at O °C, and the mixture was left for 1 hour at this temperature then at room temperature for 12 h. The silicon substrate was cleaned with acetone and toluene, and dried under a nitrogen flow. Polymerization of PNIPAAm was achieved by immersing the silicon substrate with the initiator grafted on the surface in a degassed solution of *N*-isopropylacrylamide (25 % w/v) in a 1:1 (v/v) mixture of H_2O and MeOH (5 mL) containing CuBr (0.032 g, 0.23 mmol) and pentamethyl diethylene triamine (PMDETA; 0.14 mL) for 100 minutes for all substrates. Under these conditions, the film thickness was about 44.8 ± 4.2 nm.

Laser cutter: The laser cutter used to generate microgrooves on silicon wafer was QuikLaze II (New Wave Research, USA). The wavelength and repetition rate of the laser pulse were 532 nm and 20 Hz, respectively. By adjusting the size of the rectangular laser spot and the intensity of the laser pulse, the width and depth of the microgrooves for rough silicon substrates could be controlled.

SEM and water CA measurements: A field-emission SEM (JSM-6700F, Japan) was used to obtain SEM images of the substrates. Water CAs were measured with a OCA20 machine (DataPhysics, Germany) at saturated humidity. The temperature was controlled by a superthermostat (Julabo F25, Germany).

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