ADVANCED MATERIALS

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Dual-Responsive Surfaces That Switch between Superhydrophilicity and Superhydrophobicity**

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In general, superhydrophobic surfaces[1,2] 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 of about 0° can be realized through a three-dimensional (3D)[3] or two-dimensional (2D) capillary effect[4] on hydrophilic surfaces. The surface roughness dramatically enhances the CA on the hydrophobic surface but decreases the CA on the hydrophilic surface owing to the capillary effect, which is consistent with Wenzel's equation.[5] The fundamental mechanism of these phenomena proposes that a combination of a hierarchical micro/nanostructure is essential for superhydrophilicity/superhydrophobicity. Recently, with the development of the combination of responsive materials and surface roughness,[6,7] several thermally, pH, or optically responsive smart interfacial materials that can switch between superhydrophilicity and superhydrophobicity have been reported: for example, a temperature-responsive polymer poly(*N*-isopropyl acrylamide (PNIPAAm);[6] photoresponsive materials, such as ZnO,[8] spiropyram,[8] two-level-structured self-adaptive surfaces,[9] the photoswitched wettability on an electrostatic self-assembled monolayer;[8] and a reversible pH-responsive surface.[10] However, all of these surfaces[11,12] are responsive to only one kind of external stimuli, such as temperature,[6] light,[8] or pH.[10] To the best of our knowledge, a dual-responsive surface that switches between hydrophilic and hydrophobic has never been reported, to say nothing of a dual-responsive surface that switches between superhydrophilic and superhydrophobic.

In this communication, a dual-stimuli-responsive surface with tunable wettability, reversible switching between superhydrophilicity and superhydrophobicity, and responsivity to both temperature (*T*) and pH, is reported. Such surfaces are obtained by simply fabricating a poly(*N*-isopropyl acrylamide-*co*-acrylic acid) [P(NIPAAm-*co*-AAc)] copolymer thin film on both a flat and a roughly etched silicon substrate. Reversible switching between superhydrophilicity and superhydrophobicity can be realized over both a narrow temperature range of about 10 °C and over a relatively wide pH range of about 10. This dual-responsive property is a result of the combined effect of the chemical variation of the surface and the surface roughness. In contrast to the roughness-enhanced homo-PNIPAAm film that is only responsive to temperature, the dual responsivity of the P(NIPAAm-*co*-AAc) films is due to the effective addition of the pH-sensitive component, acrylic acid (AAc). In addition, the lower critical solubility temperature (LCST) of the copolymer is tunable with increasing pH.

The copolymer P(NIPAAm-*co*-AAc) thin films are fabricated on both a flat and a rough silicon substrate by a typical surface-initiated atom transfer radical polymerization.[13] Compared with Figure 1a (left), which shows the flat substrate, Figure 1a (right) shows a typical scanning electron microscopy (SEM) image of a rough surface on which geometrical structures of patterned square pillars (20 μm high, 12 μm long, and with a spacing of 6 μm between the silicon pillars) have been introduced on a flat silicon wafer by photolithography and an inductively coupled plasma deep-etching technique. The magnified image of the rough substrate shows one of the silicon pillars (Fig. 1b). Typical atomic force microscopy (AFM) images of one of the silicon pillars before (Fig. 1c) and after polymerization (Fig. 1d) show that the latter is composed of many irregular micro/nanoparticles and pores. This copolymer consists of both a temperature-sensitive component (NIPAAm) and a pH-sensitive component (AAc). The results of X-ray photoelectron spectroscopy (XPS) and gel permeation chromatography (GPC) also provided the molecular weight and polydispersity of the copolymer and the elements on the surface (see Supporting Information).

For the flat substrate, the P(NIPAAm-*co*-AAc) thin film exhibits a dual-responsive switching between hydrophilicity and hydrophobicity. At pH 7 (Fig. 2a), the water CA increases from 69.1 ± 1.2° (*T* = 21 °C) to 82.1 ± 1.5° (*T* = 45 °C). When *T* = 34 °C (Fig. 2b), the water CA decreases from 88.4 ± 1.8°

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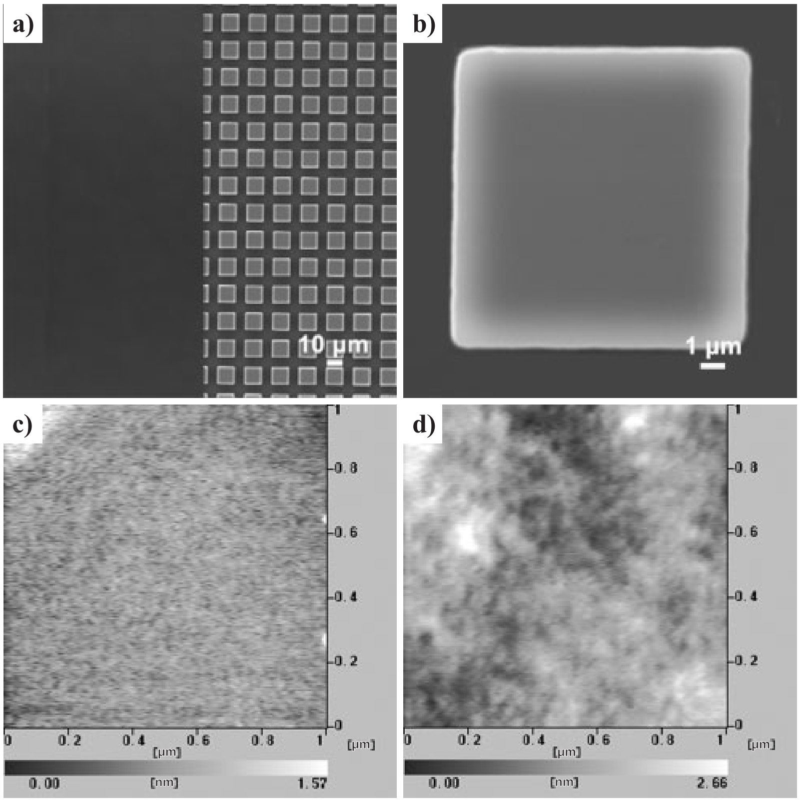

Figure 1. a) Typical SEM images of a flat and a rough substrate. b) Magnified image of one of the micropillar arrays of (a). c,d) Typical AFM images of a silicon pillar before and after polymerization, respectively.

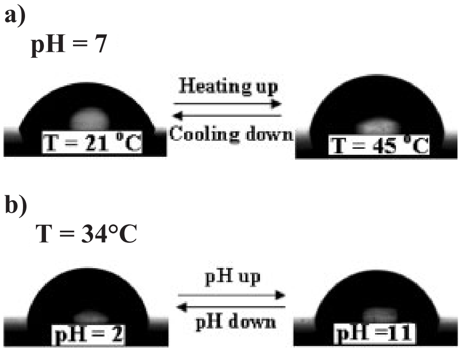

Figure 2. a) At pH 7, the CAs change with temperature. b) When $T = 34$ °C, the CAs change with pH.

(pH 2) to 78.8 ± 1.6° (pH 11). This effect is explained by the competition between intermolecular and intramolecular hydrogen bonding below and above the LCST. The switching mechanism at the rough substrate is discussed below.

Compared with the change of CAs on the flat film (less than 15°), an extremely large change of CA (about 150°) is induced on the rough substrate. Figure 3a shows how the dual-responsive surfaces work under the external stimuli (temperature and pH). The *x*-axis represents the pH value and the *y*-axis the temperature. The general trend in the change of wettability is that half of the CAs of the water profiles are almost all larger than 130° (the background color is red) and the others are almost all smaller than 20° (the background color is blue). The film is hydrophilic at low temperatures and hydrophobic at high temperatures (when the pH is fixed), which is similar to a single, thermally responsive film. Interestingly, the film simultaneously shows a very strong dependence on the pH value. That is, the film is hydrophobic at low pH, and hydrophilic at high pH.

To determine the effect of pH on the CAs for the dual-responsive films, further studies have been developed in detail and are summarized in Figure 3b. At pH 7 (the third column in Fig. 3a), the water profiles show that the film changes from being superhydrophilic to superhydrophobic at 32 °C, which is the same LCST as for homo-PNIPAAm[14] (the LCST of the copolymer here can be defined as the transition point of the CAs against temperature). This is probably due to the low content of AAc in the copolymer, which has no effect on the LCST in the neutral environment. However, at pH 4, the LCST of the copolymer is about 24 °C, while at pH 9, the LCST of the copolymer is about 36 °C. More interestingly, at pH values of 2 (the first column in Fig. 3a) and 11 (the fifth column in Fig. 3a), the water profiles show no obvious variation with the change of temperature. These phenomena can be explained as follows. At pH 2, the PAAc chain will become uncharged, and its expanded molecular coil should shrink.[15,16] Thus, the water profiles show nearly stable CAs at about 130–150°, and the LCST is considered to be less than 21 °C (the lowest temperature in the CA experiments). Correspondingly, at pH 11, the majority of the AAc components are charged, which conveys sufficient solubility to offset the aggregation of the hydrophobic temperature-sensitive components. Thus, the water profiles show nearly stable CAs of about 0°–20°, and the LCST is considered to be larger than 45 °C (the highest temperature in the CA experiments). These results indicate that the LCST of the dual-responsive copolymer can be tuned from less than 21 °C to higher than 45 °C, by simply changing the pH value from 2 to 11. The change in trend of LCST correlates with the work of Cho's group.[17] There is another useful and interesting property that arises from simultaneously controlling the pH and temperature. That is, the film is hydrophobic at low temperatures and hydrophilic at high temperatures (with different pH), which is different to the previously investigated single, thermally responsive material (see Supporting Information Fig. S2).

All these phenomena can be explained by the reversible change in hydrogen bonding between the two components (NIPAAm and AAc) and water. To thoroughly understand the dual-responsive material, theoretical considerations are

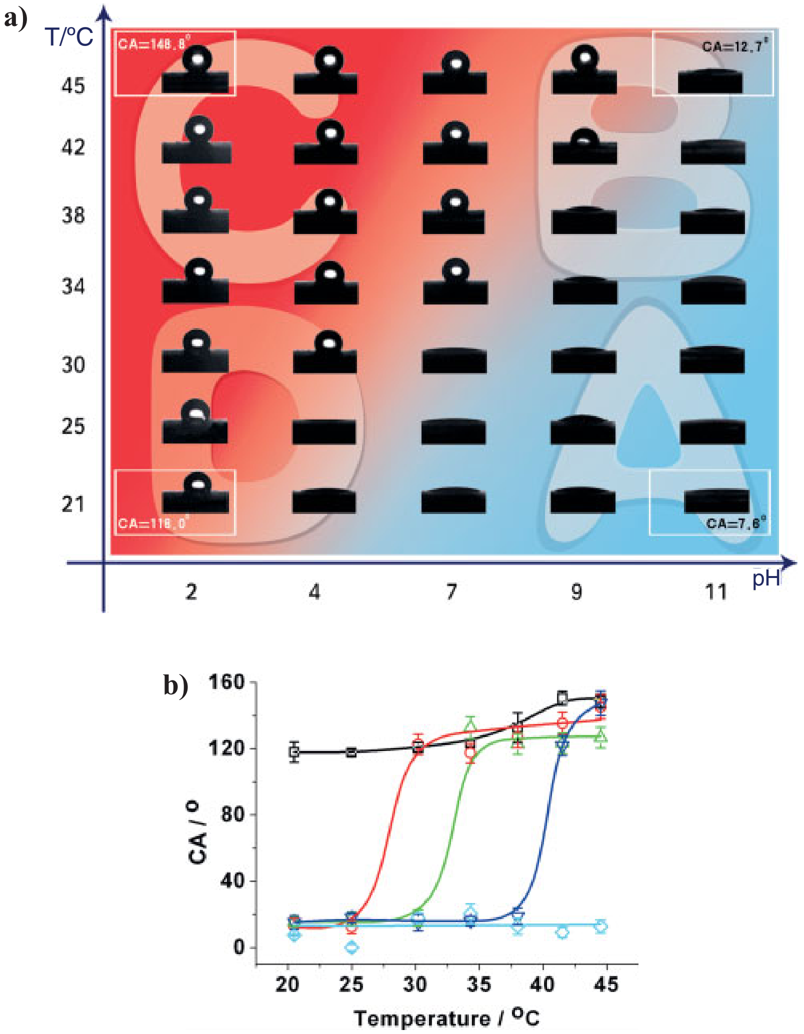

Figure 3. a) When the pH and/or temperature is varied, the CAs reversibly change (regions A–D correspond to those marked in Figure 4a). b) Temperature and pH dependence of water CAs for P(NIPAAm-*co*-AAc) thin films. Water CAs change at different temperatures for a modified substrate, at pH values of 2 (□), 4 (○), 7 (△), 9 (▽), and 11 (◇), respectively.

necessary. Hypothetical conformations of hydrogen bonding between the copolymers and water in the regions A, B, C, and D are suggested in Figure 4a, and they correspond with those in Figure 3a. In region A, both the PAAc and PNIPAAm components are at their most hydrophilic[16] (high pH and low temperature). The loosely coiled conformation of the P(NIPAAm-*co*-AAc) chains and intermolecular hydrogen bonding with water molecules lead to a high surface free energy and a small water CA. The film is hydrophilic and water enters the microgrooves beneath the water droplet.[5] In this situation, the surface roughness becomes the dominant factor that intensifies the hydrophilicity.

In region C, the AAc chain will become uncharged. Both the PAAc and PNIPAAm components are at their most hydrophobic level (low pH and high temperature). The compact and collapsed conformation[17] of the P(NIPAAm-*co*-AAc) chains, which is induced by intramolecular hydrogen bonding between C=O, N–H, and the acrylic acid groups in the copolymer chains, leads to a low surface free energy and large water CAs. The film is hydrophobic and the rough surface increases the air/water interface.[18] In this situation, the surface roughness becomes the dominant factor enhancing the hydrophobicity. Regions B,D are the transition phases. The wettability of the film is decided by the competition of the intermolecular and intramolecular hydrogen bonding. Region B remains hydrophilic: because of the hydrophobic effect of PNIPAAm at a high temperature, the CA in the top right corner of region B (12.7°) is larger than that in the bottom right corner of region A (7.6°). Region D remains hydrophobic: because of the hydrophilic effect of PNIPAAm at low temperatures, the CA in the bottom left corner of region D (118.0°) is lower than that in the top left corner of region C (148.8°). From the above, it can be seen that their is a cyclic connection between the four regions. Therefore, the dual-responsive surface responds to both temperature and pH.

The temperature and pH are repeatedly cycled, and the variation of the water CAs is recorded. The measurements of water CAs at high and low temperatures and pH are conducted on two sample stages, one set at $T = 21\,°C$ and pH 11 (region A in Fig. 3a) and the other at $T = 45\,°C$ and pH 2 (region C in Fig. 3a). The results show excellent reversibility for 20 cycles (Fig. 4b) and a quick transformation between superhydrophilicity and superhydrophobicity as a single cycle lasts only several minutes. This reversibility remains after the samples have been laid aside without special protection for at least two months, which shows that the copolymer film is stable.

In conclusion, a dual-responsive material that is responsive to both temperature and pH is fabricated. The copolymer contains temperature-sensitive and pH-sensitive components. Under external stimuli, the hydrogen bonds between the two components and water reversibly change. Therefore, the intelligent materials reversibly change between superhydrophobicity and superhydrophilicity. In addition, the LCST of the copolymer can be tuned by increasing the pH. This method can also be easily extended to other dual-responsive surfaces. This ability to control the wettability by changing the temperature and pH has applications in a broad range of fields, such as microfluidic switching,[19] drug delivery,[20] surfactants,[21] and separation.[22]

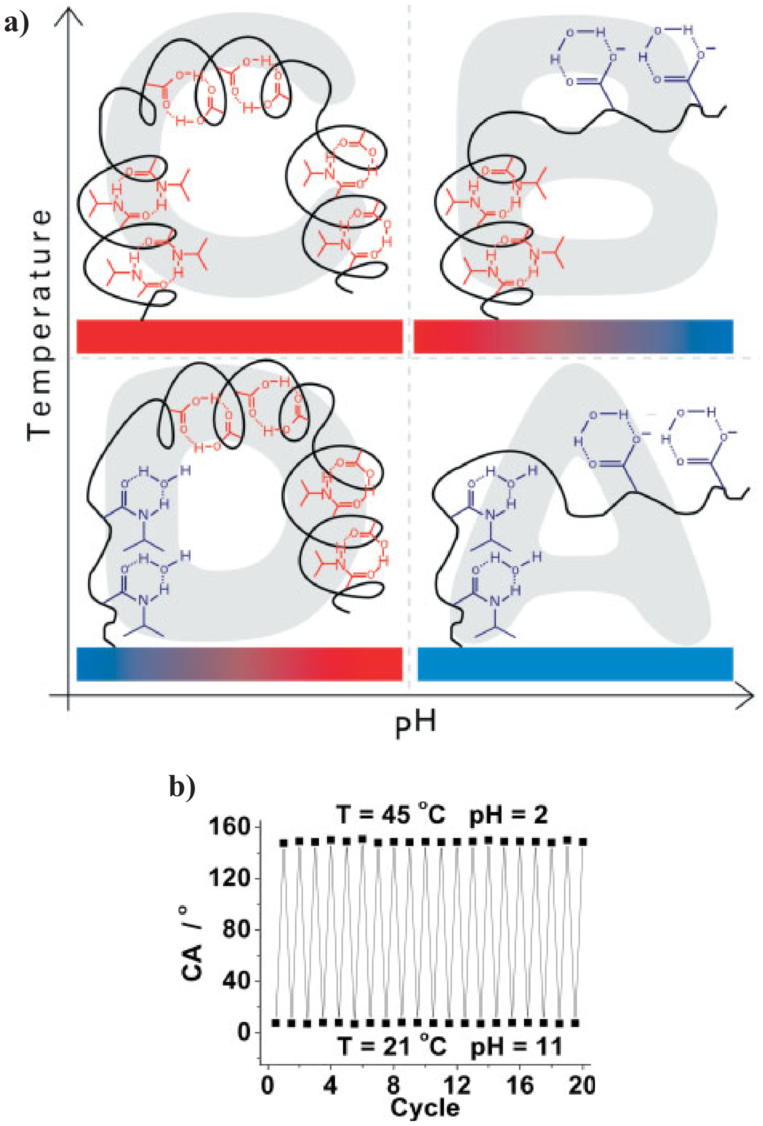

Figure 4. a) Hypothetical conformations of hydrogen bonding between the copolymers and water which reveal two kinds: the intermolecular hydrogen bonds between P(NIPAAm-*co*-AAc) chains and water molecules when the temperature is below the LCST, and the intramolecular hydrogen bond among C=O, N–H and the carboxylic acid groups in the copolymer chains when the temperature is above the LCST. (Regions A–D correspond to those marked in Figure 3a). b) Water CAs at two different temperatures and pH for a P(NIPAAm-*co*-AAc)-modified rough substrate. Half cycles: $T = 21$ °C, pH 11, and integral cycles: $T = 45$ °C, pH = 2.

Experimental

Materials: NIPAAm (Fluka, Switzerland) was recrystallized in *n*-hexane. AAc (Beijing Beihua Fine Chemical Co. Ltd., China) was purified by distillation at 40 °C/26 mm Hg. Silicon wafer (Grinm Semiconductor Materials Co. Ltd, China), acetone, nitric acid, methanol, sodium hydroxide, pyridine, α-bromoisobutyryl bromide (Fluka, Switzerland), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (Aldrich, Germany), and aminopropyl trimethoxysilane (ATMS, Fluka, Switzerland) were used as received. CuBr was recrystallized before use. Toluene and dichloromethane were dried by molecular sieves for 24 h before use. Double-distilled water (> 1.82 MΩ cm, MilliQ system) was used.

Synthesis of P(NIPAAm-co-AAc) Thin Films on Silicon Substrates: A clean silicon substrate was immersed in an aqueous NaOH solution (0.1 M) for 5 min and subsequently in HNO_3 (0.1 M) for 10 min to generate surface hydroxy 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.-% 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 any remaining ATMS, dried under a flow of nitrogen gas, and immersed in dry dichloromethane that contained pyridine (2 % v/v). The polymerization initiator, bromoisobutyryl bromide, was added dropwise into the solvent that contained the silicon substrate at 0 °C, and the mixture was left for 1 h at this temperature, and then at room temperature for 12 h. The silicon substrate was cleaned with acetone and toluene and dried under a nitrogen flow. Polymerization of P(NIPAAm-*co*-AAc) was achieved by immersing the silicon substrate, with the initiator grafted on the surface, in a degassed solution of NIPAAm (1.02 g) and AAc (0.02 mL) (3 mol-% of AAc against NIPAAm) [16] in a 1:1 (v/v) mixture of H2O and MeOH (5 mL) containing CuBr (0.032 g, 0.23 mmol) and pentamethyldiethylenetriamine (PMDETA, 0.14 mL) for 2 h at 60 °C. Under these conditions, the film thickness was between 17 and 21 nm.

Instrumentation and Characterization: A field-emission scanning electron microscope (JSM–6700F, Japan) was used to obtain SEM images of the substrates.

CAs were measured on an OCA20 machine (DataPhysics, Germany) at ambient temperature and saturated humidity. The materials were first placed in the solution (pH 2) for about 20 min, taken out from the solution, blow dried by N_2, and heated to 21 °C. Deionized water droplets (about 1 µL) were dropped carefully onto the dual-responsive surface. An average CA value was obtained by measuring the same sample at five different positions. The materials were then placed in the solutions (pH = 4, 7, 9, and 11, respectively) to test the CAs of the materials at the same temperature (21 °C). In addition, the CAs of the materials were measured at 25, 30, 34, 38, 42, and 45 °C, respectively, with the same solutions (pH 2, 4, 7, 9, 11). The results were summarized in Figure 3b.

The temperature was controlled by a super-thermostat (Julabo F25, Germany). Contact lithographic masks were constructed by Microelectronics R&D Center, the Chinese Academy of Sciences. A KARL SUSS MA6 (Germany) instrument was used to transfer the patterns of masks onto silicon wafers by a photolithographic method. A deep-etching process was completed using an STS ICP ASE (UK) instrument. AFM experiments in the tapping mode were conducted on an SPI 3800N Probe Station (Seiko Instruments Inc, Japan). A microfabricated Au-coated silicon cantilever with a bending spring constant of 0.098 N m^{-1} and a resonance frequency of 11 kHz was used for all experiments with a 100 µm scanner. All AFM experiments were performed in air.

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