Supporting Information

Building a Smart Surface with Converse Temperature Dependent Wettability Base on Poly(acrylamide-co-acrylonitrile)

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1. Materials.

Porous anodic aluminum oxide plates (AAO, Whatman, Germany; aperture size: 100 nm; diameter: 13 mm) were purchased from Shanghai Jinpan Biotechnology Co., Ltd. (Shanghai, P. R. China). Acrylonitrile (AN; AR), 2-mercaptoethanol, 1,4-bis(bromomethyl)benzene (AR) and 2,2-azobisisobutylnitrile (AIBN; AR) were provided from Beijing InnoChem Science & Technology co, Ltd. (Beijing, P. R. China). Prior to use, AAO was thoroughly rinsed using ultrasonic cleaner (KQ-300DE, Shumei, P. R. China), AN was purified via reduced-pressure distillation, and AIBN did by recrystallization from alcohol. Acrylamide (AAm, 99.9%) and carbon disulfide (99.0%) were supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, P. R. China) and directly used without further purification. Tri-potassium phosphate monohydrate (K₃PO₄.H₂O, 96%) and 1H, 1H, 2H, 2H-perfluoroocytliethoxysilane (C₁₄H₁₉F₁₃O₃Si₃, PFOTES, 98%) were supported by Adamas Reagent co, Ltd. (Shanghai, P. R. China). All other reagents and organic solvents were of analytic grade and without further purification.

Silica gel and thin layer chromatography plates (TLC, GF254; size: 25×75 mm; thickness: 0.20~0.25 mm) were produced from Qingdao Haiyang Chemical Co., Ltd (Qingdao, P. R. China). Chromatographically pure N, N-dimethylformamide (DMF) for gel permeation chromatography (GPC) was purchased by Avantor Performance Materials trading Co. Ltd. (J. T. Baker, Shanghai, U. S. A.).

2. Synthesis and characterizations of chain transfer agent (CTA)

As CTA, 1,4-Phenylenebis(methylene) bis(2-hydroxyethyl) bis(carbonotrithioate) was
synthesized according to the previously reported method. Typically, 0.550 mL of 2-mercaptoethanol (7.513 mmol) and 0.967 g of K$_3$PO$_4$•H$_2$O (4.199 mmol) were mixed in 15 mL of tetrahydrofuran (THF). Subsequently, 1.361 mL of carbon disulfide (22.52 mmol) was added dropwise into the suspension with vigorous stirring for 30 minutes, following by the slow addition of 15 mL of THF solution of 1,4-bis(bromomethyl)benzene (0.993 g, 3.762 mmol). After stirred at room temperature for 1 hour, the solid suspension was thoroughly removed by filtration. The residual solution was concentrated by rotary evaporation to obtain a yellow oily solid. The final products were purified by recrystallization in chloroform. Yield: 0.576 g (37 %).

$^1$H-NMR (600MHz, deuterated dimethylsulfoxide, namely d$_6$-DMSO; see Fig. S1): $\delta=7.35$ ppm (s, 4H), 5.13 ppm (s, 2H), 4.66 ppm (s, 4H), and 3.64 (t, 4H), 3.50 (t, $J = 6.0$ Hz, 4H), 2.50 ppm (s, d$_6$-DMSO residual peak). $^{13}$C-NMR (see Fig. S2): $\delta=224.1, 135.2, 130.0, 58.8, 40.5$ and 40.0 ppm (d$_6$-DMSO residual peak). m/z: 432.95316 (C$_{14}$H$_{18}$O$_2$S$_6^+$).

**Nuclear magnetic resonance spectroscopy (NMR)**

Both $^1$H-NMR and $^{13}$C-NMR spectra were recorded on an AVANCE NEO 600 MHz spectrometer (Bruker, Germany) using deuterated dimethylsulfoxide (d$_6$-DMSO) as solvent and tetramethylsilane (TMS) as internal standard.
Fig. S1 $^1$H-NMR spectrum of CTA

Fig. S2 $^{13}$C-NMR spectrum of CTA
Mass spectroscopy (MS)

The mass spectrum of CTA was characterized by Q-Exactive Orbitrap mass spectrometry coupled with ultraperformance liquid chromatography (Thermo Fisher, Q-Exactive, USA) at the set column temperature of 40 °C. The injection volume of sample was 10 μL. The mobile phase was chromatographic grade acetonitrile with fixed flow rate of 0.4 mL/minute.

3. Synthesis and characterizations of poly(acrylamide-co-acrylonitrile) [P(AAm-co-AN)]

Dihydroxy-terminal P(AAm-co-AN) was synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT) using 1,4-phenylenebis(methylene) bis(2-hydroxyethyl) bis(carbonotrithioate) as CTA. Typically, 2.20 g of AAm (30.95 mmol), 1.64 g of AN (30.94 mmol), 0.076 g of CTA (0.185 mmol), 8.7 mg of AIBN (0.054 mmol) and 12.3 mL of DMF were added one by one into a 50-mL Schlenk flask and mixed well by magnetic stirring. After at least three freeze-vacuum-thaw cycles, the reaction mixture was sealed and then immersed in an oil bath at 60 °C for 7 hours. Some yellow solids were obtained by three precipitation cycle in excess methanol, and then dissolved in DMF for further dialysis (molecular weight cut off: 3500 Da) against deionized water for 2 days. Finally, the products was collected by freeze drying. Yield: 1.026 g (27%).

Gel permeation chromatography (GPC)

The molecular weight of the resulting P(AAm-co-AN) was measured by GPC (e2695, Waters, U.S.A.) using polystyrene standards and chromatographically pure DMF as
elucent. The measurement was proceeded with a flow rate of 0.5 mL/minute at the set column temperature of 85 °C.

**Elemental analysis (EA)**

To decide the ratio of AAm and AN of the copolymer, the elemental analysis of the P(AAm-co-AN) was carried out. It is indicated that the content of acrylamide (AAm) and acrylonitrile (AN) are 32.5% and 67.5%, respectively. The compositions of the resulting P(AAm-co-AN) were measured via an elementary vario EL cube (Elementar, Germany). Element content: N, 20.47 %; C, 55.13 %; H, 6.716 %; S, 1.577 %; O, 16.107 %.

**Table S1.** Physicochemical properties of the resulting P(AAm-co-AN)

<table>
<thead>
<tr>
<th>Number-average Molecular Weight (g/mol)</th>
<th>Weight-average Molecular Weight (g/mol)</th>
<th>Polydispersity Index (PDI)* (%)</th>
<th>AAm* (%)</th>
<th>AN* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(AAm-co-AN)</td>
<td>43000</td>
<td>49800</td>
<td>1.16</td>
<td>32.5</td>
</tr>
</tbody>
</table>

a: determined by GPC; b: determined by EA.

**Ultraviolet-Visible spectrophotometer (UV-Vis)**

The upper critical solution temperature (UCST) of the resulting P(AAm-co-AN) was measured using an UV-Vis (UV-1750, SHIMADZU, Japan) equipped with a thermostatic water bath (CBC 5 basic, IKA, Germany) at a constant heating/cooling rate of 1 °C/minute. The optical transmittance of the light beam was recorded at 500 nm. The concentration of P(AAm-co-AN) in deionized water was 1 mg/mL. The UCST
value was defined as the temperature at which the transmittance reached 50% in the turbidity curve (see Fig. S3).

![Turbidity curve of P(AAm-co-AN) in deionized water at different temperatures (concentration: 1 mg/mL; heating rate: 1 °C/minute)](image.png)

**Fig. S3** Turbidity curve of P(AAm-co-AN) in deionized water at different temperatures (concentration: 1 mg/mL; heating rate: 1 °C/minute)

**Nuclear magnetic resonance spectroscopy (NMR)**

$^1$H-NMR spectra at different temperature were recorded on an AVANCE III 600 MHz spectrometer (available temperature range: -150 to +150 °C; Bruker, Switzerland) using deuterated oxide (D$_2$O) as solvent.

**Differential scanning calorimetry (DSC)**

The thermal behaviors of the resulting P(AAm-co-AN) was characterized by DSC (DSC1, METTLER TOLEDO, Switzerland) in pure nitrogen atmosphere with the fixed flow rate of 60 mL/minute. Typically, 7.1 mg of sample was treated in the temperature range between -15 and 200 °C at a rate of 5 °C / minute.
Fig. S4 DSC curves of P(AAm-co-AN) (7.1 mg; flow rate: 60 mL/minute; heating rate: 5 °C / minute).

4. Fabrication and characterizations of thermo-responsive smart surface.

As illustrated in Fig. 1C, 0.5 g of P(AAm-co-AN) was fully dissolved in 10 mL of deionized water above UCST, and then cooled to room temperature. Afterwards, a 200 μL droplet of P(AAm-co-AN) aqueous suspension was placed onto a clean polycrystalline plate, and pressed down by an AAO template for 1 hour. Here the suspension was completely penetrated into the AAO template by capillarity. The middle sample was heated up to 70 °C for 2 hours inside an electric thermostatic drying oven (DZF-6020, Jinghong, Shanghai Jing Hong Laboratory Instrument Co., Ltd., Shanghai, P. R. China). Similarly, the P(AAm-co-AN)-coated side of the sample was pressed down on a 200 μL droplet of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (C_{14}H_{19}F_{13}O_{3}Si_{3}; PFOTES) for 15 minutes. The final thermo-responsive smart surface
was obtained by rinsing ten times with anhydrous ethanol and subsequently heating to 100 °C for 1 hour. The same process was also used for preparing the control surfaces on the flat glass substrates.

*Fourier transform infrared spectroscopy (FT-IR)*

The attenuated total reflection (ATR) spectra of the smart surface at different temperatures were recorded using a FT-IR spectrometer (VERTEX 70, Bruker, Germany) equipped with a smart variable temperature accessory (025-4018, Bruker, Germany), in a spectral range of 4000–400 cm⁻¹ with the resolution of 2 cm⁻¹.

*Scanning electron microscope (SEM)*

The morphologies of AAO template and smart surface were photographed by a field emission scanning electron microscope (Gemini 500, ZEISS, Germany).

![Cross-sectional SEM images of the crude AAO substrate and the UCST-type surface.](image)

**Fig. S5** Cross-sectional SEM images of the crude AAO substrate and the UCST-type surface.
Surface profile analysis

The layer thickness, surface topography and roughness were measured by three-dimensional (3D) surface profiler (DCM8, Leica, Biberach, Germany) with a 50-fold objective.

![Fig. S6 3D surface topography of the AAO substrate (Ra= 0.06 μm; A) and the UCST-type surface. (Ra= 0.188 μm; B)](image)

Contact angle meter

2 μL of deionized water droplet was dripped onto the resulting smart surface and heated up to different temperatures using a smart variable temperature accessory (025-4018, Bruker, Germany). Till the static water contact angles (WCA) kept stable at a determined temperature, the real-time images of the water droplet were recorded and analyzed via. a contact angle meter (Dataphysics OCA 20, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd., P. R. China). Every contact angle was measured at least three times and averaged. The variation of WCA (ΔWCA) is defined as the difference between the original (θ₀) and the resulting equilibrium WCA (θ₁), namely...
$\Delta \text{WCA}(\degree) = \theta_1 - \theta_0$. Further, the response rate was calculated using the following equation:

$$\text{response rate} (\degree/\text{s}) = \frac{\Delta \text{WCA} (\degree)}{\text{response time} (\text{s})}$$

where the responsive time is defined as the time needed for the whole change from $\theta_0$ to $\theta_1$. All the corresponding results were listed in Table S2.

### Table S2. Response parameters of UCST-type smart surface

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\theta_0$</th>
<th>$\theta_1$</th>
<th>$\Delta \text{WCA}$</th>
<th>Response Time</th>
<th>Response Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>112.0°</td>
<td>103.4°</td>
<td>8.6°</td>
<td>10.86 s</td>
<td>0.79°/s</td>
</tr>
<tr>
<td>40 °C</td>
<td>106.9°</td>
<td>97.3°</td>
<td>9.6°</td>
<td>4.84 s</td>
<td>1.98°/s</td>
</tr>
<tr>
<td>50 °C</td>
<td>94.5°</td>
<td>76.7°</td>
<td>17.8°</td>
<td>3.46 s</td>
<td>5.14°/s</td>
</tr>
<tr>
<td>60 °C</td>
<td>87.1°</td>
<td>65.0°</td>
<td>22.1°</td>
<td>3.35 s</td>
<td>6.60°/s</td>
</tr>
<tr>
<td>70 °C</td>
<td>88.4°</td>
<td>62.4°</td>
<td>26.0°</td>
<td>2.84 s</td>
<td>9.15°/s</td>
</tr>
<tr>
<td>80 °C</td>
<td>87.1°</td>
<td>60.1°</td>
<td>27.0°</td>
<td>2.42 s</td>
<td>11.16°/s</td>
</tr>
</tbody>
</table>

**Note:** “s” is the abbreviation of a time unit, “second”.

### Table S3. Quantitative comparison on responsive rate between LCST-type and UCST-type surfaces.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Response rate (°/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>0.32 (20 °C, below LCST)</td>
<td>Ref. [3]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>0.83 (room temperature, below LCST)</td>
<td>Ref. [4]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>0.5  (room temperature, below LCST)</td>
<td>Ref. [5]</td>
</tr>
<tr>
<td>P(AAm-co-AN)</td>
<td>6.60 (over UCST)</td>
<td>This work</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>
**Table S4.** Quantitative comparison on cycle number between LCST-type and UCST-type surfaces.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cycle Numbers</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>5</td>
<td>Ref. [6]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>5</td>
<td>Ref. [7]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>5</td>
<td>Ref. [8]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>5</td>
<td>Ref. [9]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>3</td>
<td>Ref. [10]</td>
</tr>
<tr>
<td>PNIPAM (LCST-type)</td>
<td>5</td>
<td>Ref. [11]</td>
</tr>
<tr>
<td>P(AAm-co-AN)</td>
<td>6</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Fig. S7** FT-IR spectra of the control surface on the flat glass substrate before (black line) and after (red line) PFOTES modification.
**Fig. S8** Response curves of the control surfaces: only PFOTES modified (black line), only P(AAm-co-AN)-modified (blue line) and P(AAm-co-AN)/ PFOTES co-modified glass substrate (red line).
**Video S1** WCA variations on UCST-type surface at 30, 60 and 80 °C.

(see the attached video file named “WCA variations on UCST-type surface at 30, 60 and 80 °C”)

References


