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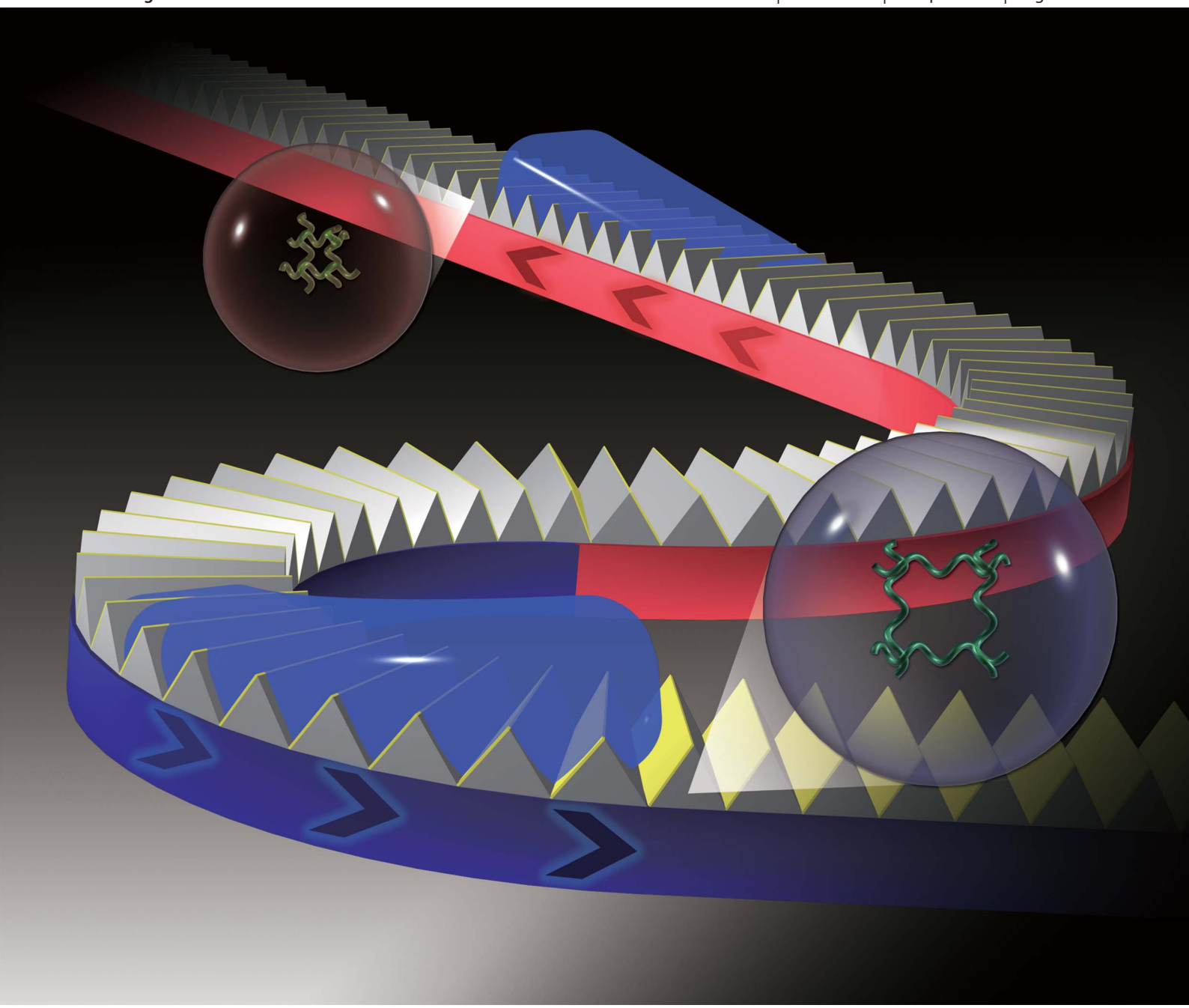

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We present a simple approach to reversibly switch the direction of liquid flow on physically symmetric and chemically asymmetric prism structures by exploiting the reversibility of surface wetting properties of a thermo-responsive polymer, poly(*N*-isopropyl-acrylamide). Such an asymmetric prism array creates a flow path in the direction of the lower critical contact angle. This allows a unidirectional "step flow" across the ridges of prism channels, which can be made reversible with a suitable temperature change.

Recently, directional wetting and flow of liquid has received much attention for its potential use as a way of controlling liquid flow in microfluidics and water harvesting.[1–22] Previous studies have mostly dealt with unidirectional liquid wetting or spreading on asymmetric microstructures. In one approach, inclined nanostructures in the form of stooped nanopillars[1–3] or inclined nanorods[4,5] have been utilized for the unidirectional wetting. In others, the directional liquid spreading has been made possible with spatial gradients or anisotropic structure.[6–22]

A basic question we raised regarding the unidirectional spreading and wetting is whether the unidirectionality can be made reversible with the same structure. That is to say that if the spreading is unidirectional in one direction on a given structure, could we make it unidirectional in the opposite direction on the same structure? A related intriguing question is whether this reversibility can be realized on demand. Directionality necessarily requires anisotropy in terms of structure or gradient.[1–22] The very nature of anisotropy, so much relied on for directionality, negates its use for the reversible directionality. For the reversibility, therefore, a macroscopic, left-right symmetry in structure is needed. On the other hand, there has to be a force acting on the liquid for the liquid front to advance in the desired direction. Within the overall symmetry, therefore, anisotropy is needed to generate such a driving force.

To address these issues, we present herein a designed structure with physical symmetry and chemical asymmetry for reversible and unidirectional step flow of liquid. The resulting structure is an array of equilateral triangular micro-prisms consisting of thermo-responsive polymers, only one face of which is covered with metal films (*i.e.*, a two-face prism array). Because of the difference in the critical contact angle on the two surfaces, the liquid flows unidirectionally and the direction could be switched by exploiting the changes in wetting properties of thermo-responsive polymers with the control of temperature.

Fig. 1a schematically shows the procedure involved in fabricating a two-face prism array. To switch the chemistry of the surfaces, we used ultraviolet (UV)-curable poly(*N*-isopropylacrylamide) (PNIPAAm), which is a well-known thermo-responsive polymer[23–31] that switches from hydrophobic to hydrophilic below its Lower Critical Solution Temperature (LCST) of ~32 °C. The prepolymer solution to fabricate the PNIPAAm prism structures was prepared by combining *N*-isopropylacrylamide (NIPAAm), *N*,*N*-methylene-bis-acrylamide (MBAAm), ethanol, and 2-hydroxy-2-methylpropiophenone as a photoinitiator, in the weight ratio of 20 : 1 : 30 : 1.[29,30] The liquid prepolymer was dropped onto a prism shaped polydimethylsiloxane (PDMS) mold, and an original master to replicate the PDMS mold had been prepared by mechanical machining.[32] After crosslinking by 10 min exposure to UV light (5.5 mW cm^{-2}, Minuta Tech.), a cured PNIPAAm prism array was detached from the PDMS mold, and thin platinum (Pt)

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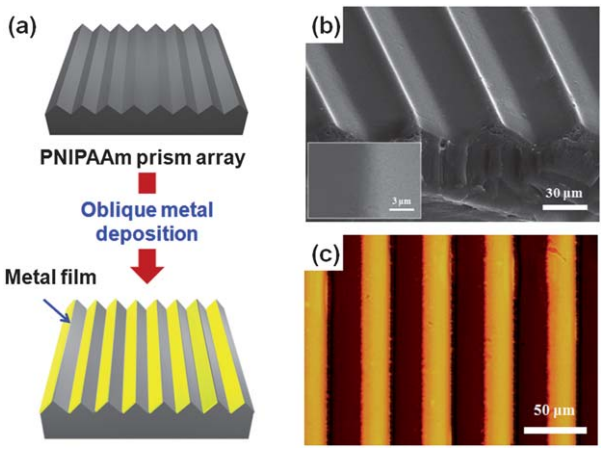

Fig. 1 (a) A schematic illustration of the fabrication of a two-face prism array. (b) SEM image of a prism array showing the symmetric structure in microscale. The inset shows a magnified SEM image of the prism array with chemical asymmetry. (c) An optical microscope image showing the left faces of the prisms covered with metal films.

metal films of ~20 nm were then deposited on only one face of the prism by oblique deposition.[32–37] Fig. 1b shows a scanning electron microscope (SEM) image of the two-face prism array used here. As seen from Fig. 1b, the period is 50 μm with a typical prism angle of ~45° at both faces.[32] A magnified view in the inset of Fig. 1b and an optical microscope image in Fig. 1c demonstrate that the prism has the structural symmetry in microscale and, at the same time, chemical asymmetry due to the metal films selectively deposited on the left faces of the prism array.

To demonstrate the directional liquid flow on the two-face prism array, we placed a water droplet on the structure and increased the liquid volume at a constant feeding rate of 1 μl min^{-1}. Fig. 2a shows the movie cuts of liquid flow moving toward the right direction. Interestingly, the liquid flow shows a step-wise movement with typical stick-slip behaviour,[1] as shown in the insets of Fig. 2a. The magnified images demonstrate that the wetting can be described by the Wenzel state because the liquid droplet fills the entire micro-prism array. As the volume of the water droplet is increased, the moving liquid front becomes pinned at the ridge until the liquid droplet overcomes the energy barrier against the movement. Then, the water front quickly steps over the ridge to the next prism valley, being pinned again. Such a cycle of pinning and step-over is repeated for the flow across the ridges of channels created by the prism array. In this sense, the unidirectional flow presented here could be termed the "step flow". The characteristics of this step flow shown in Fig. 2a are well represented in the ESI Movie 1.† It is noted that the water front moves unidirectionally toward the metal-free PNIPAAm surface. It is also noted that the step flow was also observed on a different prism array of 25 μm pitch (see Fig. S1†), suggesting that the directional flow could be achieved with a smaller feature size.

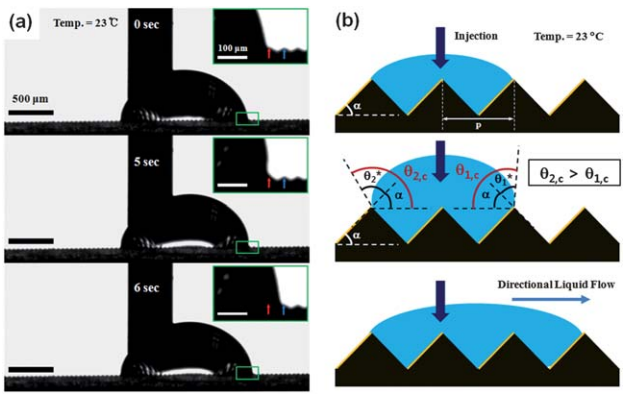

Fig. 2 (a) Movie cuts at various times showing the unidirectional liquid step flow. The water front is moving unidirectionally toward the metal-free PNIPAAm surface (right face). It is noted that the black column on the liquid is a needle of the equipment for feeding water at a constant rate. The inset in each image shows the corresponding magnified image at the three-phase contact line where the colored arrows indicate the location of ridges. (b) A schematic illustration explaining the mechanism of the directional step flow across channels formed by the prism array.

Fig. 2b is a schematic illustration of the mechanism involved in the directional liquid flow, with the three-phase contact line across the ridges of channels created by the prism array. As discussed earlier, the moving liquid front is pinned at the channel ridge and the pinning is maintained even on increasing the liquid volume until the contact angle of the liquid front reaches its critical contact angle at the edge. The critical contact angle θ_c can be written as follows:[38,39]

$$\theta_c = \theta^* + \alpha \quad (1)$$

where θ^* is the equilibrium contact angle on a planar surface or the intrinsic contact angle and α is the angle subtended by the two prism surfaces forming a solid edge, which is referred to as the edge angle. θ_1^* is the contact angle on a planar PNIPAAm surface (right face) and θ_2^* is the angle on a metal-deposited planar surface (left face). A detailed explanation is given in the ESI of Fig. S2.† In the two-face prism system, the critical contact angles of the two faces are different from each other because of their different surface chemistry. As a result, the critical contact angle is higher on one side or one face (*i.e.*, the left side of the prism array in Fig. 2b in the current case) than on the other and the liquid front is forced to move in the direction of the lower critical contact angle (*i.e.*, the hydrophilic PNIPAAm surface in this case) as the liquid volume is increased.

It is well known that the liquid flows spontaneously and preferentially along the sidewalls of grooves or channels.[38,39] A distinct difference in our work is that the liquid moves across or over the ridges of prism channels by cutting the prism sheet to a narrow strip of ~1.5 mm in width, as shown in the ESI of Fig. S3.† In this way, the liquid flow can be confined within the strip (direction 1 or 2 in Fig. S2†). Such a confined flow is beneficial for the controlled one-dimensional directional flow since the liquid front cannot spill over the lateral edges. That is, the critical contact angles at both sharp edges are always higher than the other two critical contact angles at the channel ridges (*i.e.*, the angle of the sharp edge is 90°).

To change the direction of the lower critical contact angle, we employed the reversible switching of wetting properties of a thermo-responsive polymer, PNIPAAm, which switches its surface properties from hydrophobic to hydrophilic due to the competition between intermolecular and intramolecular hydrogen bonding below and above the LCST.[23–31] Fig. 3 shows the changes in CA on flat PNIPAAm and Pt-deposited surfaces with temperature cycles between 23 °C and 40 °C. As shown in Fig. 3a, the CA on the flat PNIPAAm surface is reversibly changed from ~45.4° (±1.5°) at ambient temperature (~23 °C) to ~72.0° (±2.0°) at ~40 °C (above the LCST of ~32 °C) without additional chemical treatment. In contrast, almost a constant CA of ~61.4° (±1.4°) was observed on the Pt-deposited surface regardless of temperature cycles. As shown in Fig. 3b, the CA on the Pt-deposited surface is located between the CAs on the PNIPAAm surface at temperatures below and above the LCST. When applying the temperature-dependent CA change to the two-face prism array, the PNIPAAm surface (right face) can exhibit lower or higher critical CA (θ_c) than the CA of the Pt-deposited face (left face) depending on the substrate temperature. By utilizing these unique wetting characteristics of the two-face prism array, we could switch the direction of the lower critical CA by changing the substrate temperature.

Fig. 4a shows a schematic illustration of the change in the direction of liquid flow on the two-face prism array at two different temperatures of 23 and 40 °C. At 23 °C, the liquid flows towards the PNIPAAm face (right direction) at a feeding rate of 6 μl min^{-1} with a lower critical contact angle of ~91.8° (theoretical value: ~90.4°) (Fig. 4b). Remarkably, the direction of the liquid flow was reversed towards the Pt-deposited face (left direction) when the substrate temperature was switched to 40 °C. In this case, the lower critical contact angle to the left direction was ~132.0° (theoretical value: ~117.0°) as shown in Fig. 4c. Due to the hydrophobic nature of the surface at higher temperature, the speed of liquid flow was decreased at the same feeding rate. These characteristics of the step flow are well represented in Fig. S4.† Such a reversal of the flow direction was repeated more than five times, in good agreement with the expected wetting behavior. It is noted that the liquid flows in both directions on a symmetric PNIPAAm prism array (Fig. S5†), suggesting that the directionality is originated from the asymmetric nature of surface properties.

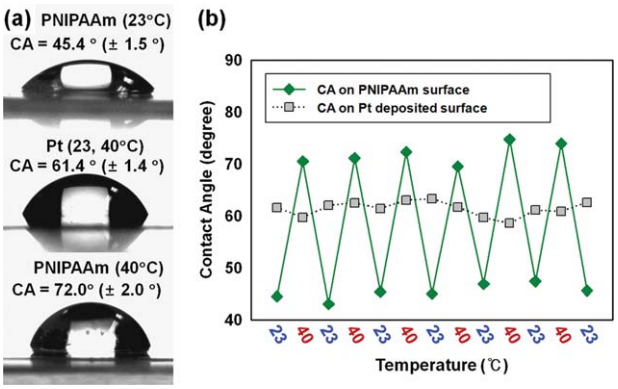

Fig. 3 (a) Images of water droplets on PNIPAAm and Pt-coated surfaces under two temperature conditions (23 and 40 °C). The contact angle (CA) on the PNIPAAm surface changes from 45.4° to 72.0° after the increase in temperature to 40 °C, while the CA on the Pt surface remains at ~61.4° at both temperatures. (b) A graph showing the reversible switching of CA on the PNIPAAm surface with temperature cycles along with CA variations on the Pt-coated surface.

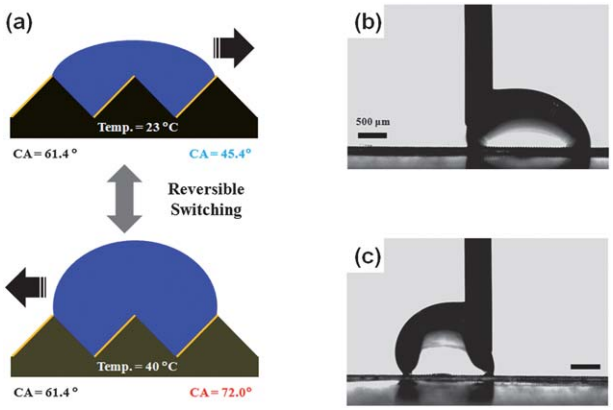

Fig. 4 (a) A schematic illustration of the change in the direction of the lower contact angle. (b) A movie cut showing the directional liquid flow on the two-face prism array at 23 °C. Water flows toward the less hydrophobic, PNIPAAm surface with an apparent contact angle of ~91.8°. (c) A movie cut showing the directional liquid flow at 40 °C. The direction of liquid flow is reversed, toward the direction of the Pt-deposited surface with an apparent contact angle of ~132.0°. The same experiments were repeated more than five times.

In summary, we have presented a simple approach to reversibly switch the direction of liquid flow by temperature change with a thermo-responsive PNIPAAm structure. An array of micro-prisms, which is physically symmetric and chemically asymmetric, gives rise to a unidirectional liquid flow across the ridges toward the lower critical CA. This allows the unidirectional "step flow" across ridges of prism channels. By changing CAs of thermo-responsive polymer surfaces, we could switch the direction of liquid flow reversibly by varying the substrate temperature. The reversible switching of flow direction would be applicable to guide a flow in microfluidic devices without using closed channels (*i.e.*, open channels) or harvest water in a more efficient way.

Experimental

Fabrication of the PNIPAAm patterned prism array

The masters used in the present study were prepared mechanically. First, a blank roll or plate of stainless steel electroplated by nickel was prepared. The blank roll or plate surface was machined by a diamond-cutting tool with a specific angle. In this process, the pitch and angle of carved patterns correspond to those of the diamond tool. The height of the patterns depends on the cutting depth of the diamond tool. In this study, a prism master with 50 μm in period and 45° in prism angle was used. After the preparation of the master, a mixture of base and curing agent (10 : 1 w/w) of Sylgard 184 PDMS elastomer was poured onto the patterned masters and cured at 70 °C for 2 h. The cured PDMS molds were peeled off from the master and cut prior to use. Drops of a PNIPAAm prepolymer solution (mixture of

N-isopropylacrylamide (NIPAAm), *N*,*N*-methylene-bis-acrylamide (MBAAm), ethanol, and 2-hydroxy-2-methylpropiophenone as a photoinitiator, in the weight ratio of 20 : 1 : 30 : 1) were dispensed onto the prism shaped polydimethylsiloxane (PDMS) mold, and a flexible PET film, ~50 μm thick, was placed on top of the mould and lightly pressed against the moulding liquid (PNIPAAm) for a supporting backplane. The PNIPAAm liquid was then exposed to ultraviolet light for 10 min, with an intensity of 5.5 mW cm^{-2} (Minuta Tech.). Subsequently, the cured polymer replica was removed from the master.

Oblique metal deposition

The polymer prism array (50 μm in period, 45° in prism angle) was coated with ~20 nm thick Pt metal on one side of the prism using only oblique metal evaporation. We used a magnetron sputter for the metal deposition and placed the polymer prism array on an inclined holder with an angle of 60°. The inclined holder defines the oblique incidence angle, resulting in the deposition of metal layers on only one side of the prism array. The two-face prism array thus fabricated had an area of 3 × 3 cm^2 and was cut to a narrow strip of ~1.5 mm width.

Physical measurements

Magnified optical images through the two-face prism array were obtained using an optical microscope (Olympus IX70, Japan). SEM images were taken using a FESEM (Hitachi S-48000, Japan). Liquid flow movie cuts on the two-face prism array were obtained by a contact angle analyzer (KRUSS DSA 100, Germany).

Acknowledgements

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