In Situ Realization of Asymmetric Ratchet Structures within Microchannels by Directionally Guided Light Transmission and Their Directional Flow Behavior

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Recently, asymmetric structures inspired from Mother Nature have received extensive attention because of their unique physical properties, such as directional wetting, directional adhesion, and directional transmission for their applications in microfluidic devices, dry adhesives, and three-dimensional displays.[1–14] More specifically, directional wetting has been reviewed in detail several times for their potential use in microfluidics and biomedical devices.[1–3] For example, Kim et al.[4] demonstrated that *"stooped"* nanohairs could control the fluid velocity within microchannels and Malvadkar et al.[5] developed slanted nanorods for drag reduction on nanofilms. These achievements have been expected to control liquid flow in microfluidic assays, in which sequential delivery of multiple reagents in detection regions and temporally controlled reagent transport are strongly needed.[15–17] Although many researchers have developed different versions of fabrication methods to realize the asymmetric structure, we are still in need for improved techniques to integrate the asymmetric structures within microchannels in simple and economic ways because the integration process of patterned structures within microfluidic channels is typically complicated. For example, bonding and sealing processes of microchannels on the asymmetric patterns with precise alignment should be required. Here, we present a direct and facile method to realize programmed asymmetric structures within microchannels by combining photo-polymerization with the directional transmission through an optically asymmetric film named as the *Lucius* prism array,[7,13] which is a prism array with one facet sides coated with metal films. The Lucius prism array can refract incident rays with an angle through one facet sides of the prism array while light from the other sides for the prism is reflected off the coated metal films. By selective and directional UV exposure through the prism array onto photo-curable prepolymers filled within a microchannel, one can obtain polymeric asymmetric structures within the channel after removing uncured prepolymers. The novelty of the proposed direct integration with the Lucius prism array is the ability to control angled directions in judiciously designed prism areas by one-step photo-polymerization. Furthermore, we demonstrate two examples of the direct integration of asymmetric structures within microfluidic channels to control the fluid speed on asymmetric ratchet surfaces as well as the rate-dependent channel filling showing different dwell times in a split channel.

Figure 1 shows a schematic illustration on the direct realization of asymmetric structures using a Lucius prism array. At first, a microfluidic channel (3 mm in width and 200 μm in height) made of poly(dimethyl siloxane) (PDMS) was prepared. After making a microchannel pattern with the conventional photolithography, we cast a mixture of PDMS precursors (Sylgard 184, Dow Corning) onto the photoresist pattern. PDMS curing at 60 °C was then performed at a mixing ratio of 10:1 (prepolymer: curing agent). After the cure, the PDMS channel was detached from the photoresist pattern. The PDMS channel was then glued onto a glass plate (150 μm in thickness) with two holes for liquid injection. To create polymeric structures within the microchannel, we filled the channel with low-viscosity UV-curable polyurethaneacyrlate (PUA) prepolymers.[18] In order to guide UV light with a defined direction, an optically asymmetric Lucius prism array was placed between the light source and a photomask, as shown in Figure 1a. The Lucius prism array was prepared by the micro-molding with UV curable polymers (PUA, 311RM),[19,20] followed by the oblique metal deposition to coat metal films only on one sides of the prism array. The detailed procedure to prepare the Lucius prism arrays can be found elsewhere.[7,13] Because the left faces of the prism array are blocked by metal films, the straight incident light is bent toward the left direction, as shown in Figure 1b.

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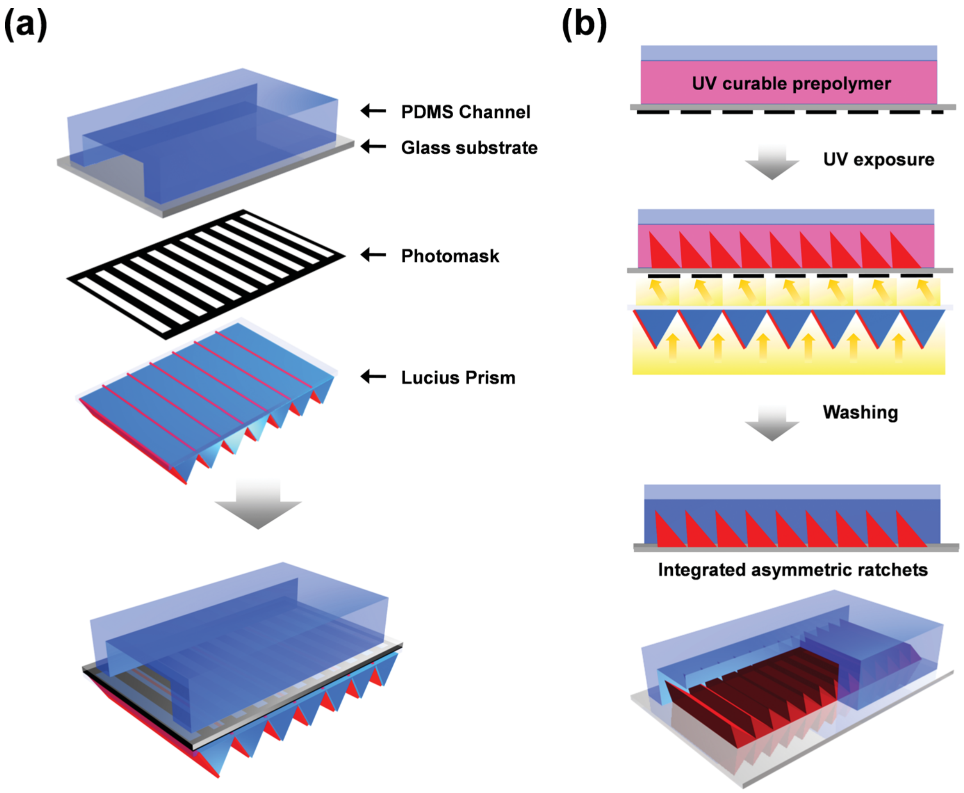

Figure 1. (a) An overall scheme for the integration of asymmetric structures within a microchannel, which is composed of a PDMS channel on a glass substrate, a photomask and the *Lucius* prism array. (b) A schematic illustration of the realization of asymmetric structures in a microfluidic channel by the guided transmission through the Lucius prism array.

After slanted UV exposure (with 365 nm in wavelength and an intensity of 400 mJ/cm^2) of the PUA prepolymers trapped within the microchannel, the unreacted PUA prepolymers were removed by rinsing with DI water several times. The asymmetric ratchets, created within the microchannel, were then dried in an oven for more than 4 hours.

Figure 2 shows scanning electron microscopic (SEM) images of a symmetric structure generated within a microchannel without using the *Lucius* prism array (Figure 2a) as well as an asymmetric structure created with the *Lucius* prism array (Figure 2b). The designed photomask lines have a width of 40 µm with a spacing of 40 µm. Figure 2b demonstrates the photopolymerized asymmetric structure created from the same mask pattern when the *Lucius* prism array was placed just below the mask. It is noted that the tilt angle is 21°, which is in good agreement with the Snell's law, as we discussed in the previous paper.[13] We further notice that the line mask pattern yielded the symmetric triangular polymer structure even without the *Lucius* prism array after curing, presumably due to non-uniformity of UV intensity within the microchannel filled with PUA prepolymers. The simulation on the light path in the presence of the Lucius prim array is given in the Supporting Information Figure S1.

To demonstrate the unidirectional liquid flow on the asymmetric ratchet structure created within a microchannel, we made an inlet hole at the center of the channel and dispensed water, colored in red, by gravity. When the water is in contact with the symmetric structure within the microchannel, water flows on both directions, as shown in Figure 2a. On the contrary, when the colored water is forced to touch the asymmetric ratchet structure, water selectively flows toward the right direction, as shown in Figure 2b. The average speed of the liquid flow was ~14 µm/s and the flow direction selected on the ratchet structure is toward the face with a lower base angle, as shown in Figure 2c.

To elucidate the different behavior of liquid flow on the asymmetric ratchet surface, we simply set the asymmetric structural model with two base angles of θ_1 (~27°) and θ_2 (~59°), as shown in Figure 2c. The retention force at a contact line prevents liquid from moving forward, which is expressed below:[21]

$$f_i = w\gamma(\cos\theta_{ri} - \cos\theta_{ai}) \quad (1)$$

where f_i is the retention force that resists the incipient motion of liquid acting on the ith direction, w is the width of a microchannel related to the length of contact line, γ is the surface tension of a liquid (i.e., water in the current case), θ_{ri} is the receding contact angle component in the ith direction while θ_{ai} is the advancing contact angle component in the ith direction. In our system, the change of liquid quantity in the reservoir is negligible despite the liquid flow through the microchannel. Hence, we can assume the receding contact angle as zero. Then, the retention force can be modified as the following:

$$f_i \sim w\gamma(1 - \cos\theta_{ai}) \quad (2)$$

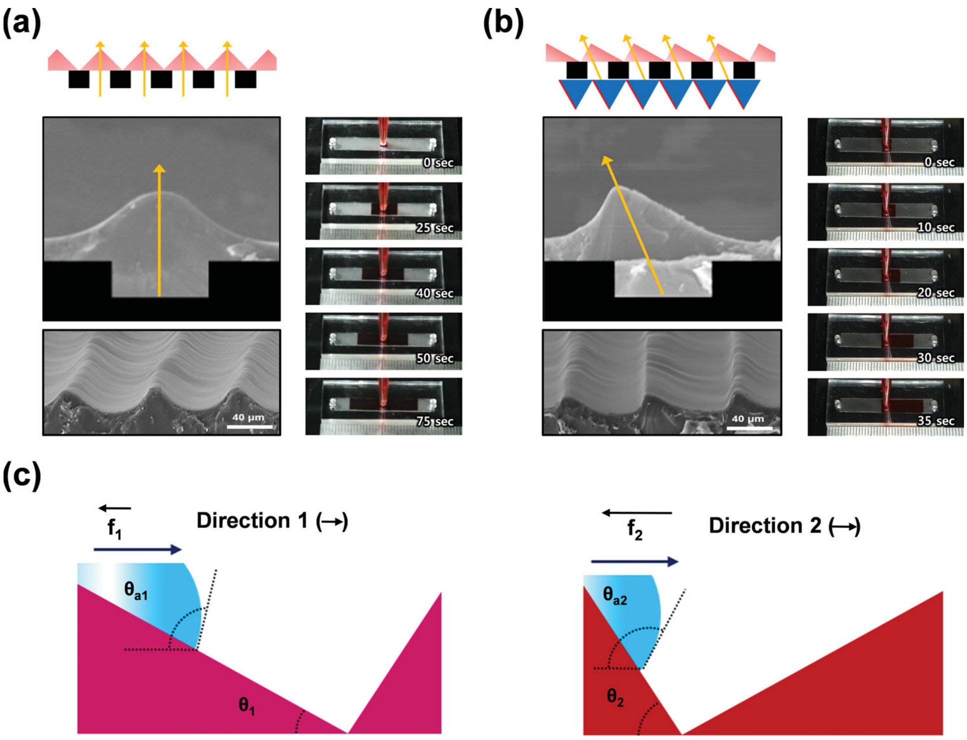

Figure 2. SEM images of polymeric structures realized within microchannels after UV illumination and representative movie cuts showing the liquid flow on the structures created within the microfluidic channels. (a) A liquid flow on a symmetric triangular pattern fabricated without a Lucius prism array. (b) A unidirectional liquid flow on an asymmetric ratchet realized with a Lucius prism array. (c) A simplified model to explain the flow velocity difference by the resistant retention force depending on contacting surfaces with different base angles.

In addition, on the face of ratchet-like structure, the advancing contact angle of the contact line is further increased by θ_i with respect to the advancing contact angle on a flat surface (θ_{a0} : ~83.1°).

$$f_i \sim w\gamma(1-\cos(\theta_{a0}+\theta_i)) \tag{3}$$

Since we apply a constant external force f_{ext} ($= P_{ext} \times w \times h$, P_{ext} and h is the external pressure and the channel height, respectively) on the liquid, the net force f_{net} is just the difference between the external force and the retention force ($f_{net} = f_{ext} - f_i$). The net force ratio (K) for the asymmetric ratchet-like structure is defined as:

$$\begin{aligned} K &= (f_{ext}-f_2)/(f_{ext}-f_1) \\ &= [1-(1-\cos(\theta_{a0}+\theta_2)(\gamma/h)/P_{ext})] \\ &\quad \times /[1-(1-\cos(\theta_{a0}+\theta_1))(\gamma/h)/P_{ext})] \end{aligned} \tag{4}$$

When we set the external pressure and the surface tension to 0.7 kN/m^2 (the gravity of water of 7 cm in height) and 0.0717 N/m^2 [22,23] respectively, the K ratio of 0.27 was obtained for the asymmetric structure created in Figure 2b. This implies that the net force in the direction 1 (flow right) is bigger than the force in the direction 2 (flow left), indicating a smaller resistance with a smaller base angle when liquid flow starts. We also note that the ratio K is independent of the channel width as shown in Equation (4) with confirming data given in the supporting information (Figure S2). Also, the retension force could be negligible in comparison with the external pressure when the surface tension of liquid is quite low (i.e., 0.0217 N/m^2 for isopropyl alcohol (IPA), as demonstrated in Figure S3.[22,23] From this observation, it is interesting that it is only the structural asymmetry that could differentiate the flow velocity with the difference in resistance. We also noted that the direction of liquid flow is determined by the critical contact angle, as discussed in the previous study.[7,24] The critical contact angle θ_c can be written as follows:

$$\theta_c = \theta^* + \alpha \tag{5}$$

where θ^* is the equilibrium contact angle on a planar surface and α is the angle subtended by a ratchet structure forming a solid edge, which is referred to as the base angle. In the present case, θ^* is the same as the bi-directions because the surface-forming material is the same all over the surface. In the asymmetric ratchet system, the critical contact angles of two faces are different from each other because of their different edge angles.[21,24–26] As a result, the critical contact angle is higher on one side when compared with the other and the liquid front is forced to move in the direction of a lower critical contact angle.

This strategy of realizing asymmetric structures within a channel with a *Lucius* prism array could easily be extended to control the speed of liquid flow with a predesigned optical *Lucius* film. **Figure 3** demonstrates an one-step procedure to create a ratchet structure with different orientations with a predesigned *Lucius* prism array. We could easily control or program the direction of ratchet orientation in a designated area within a channel with the change in the faces coated by metal

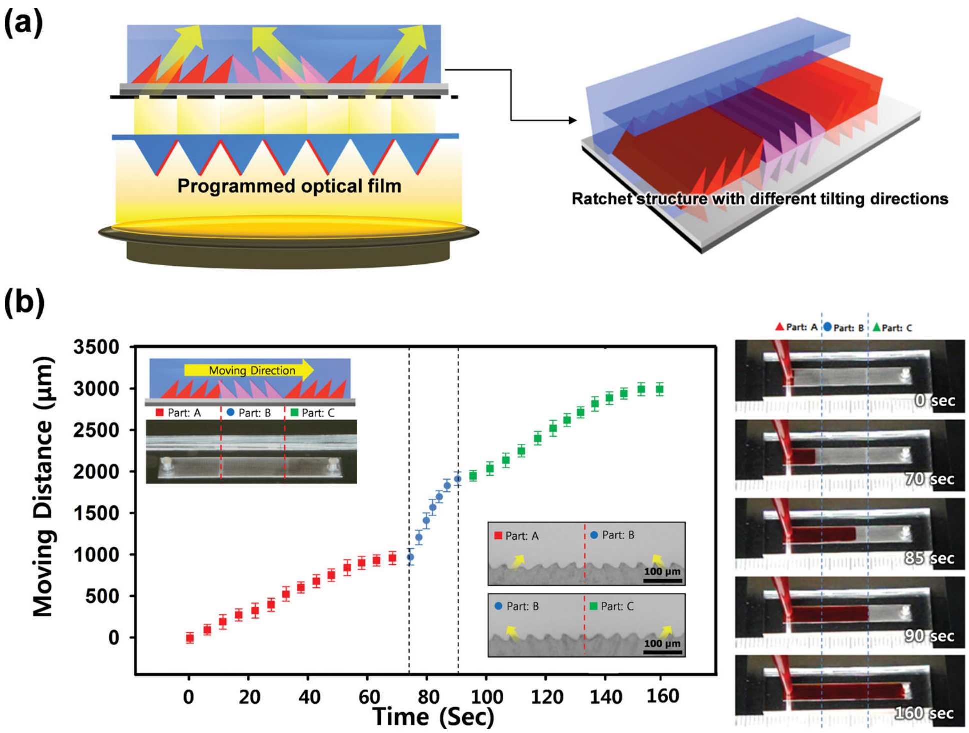

Figure 3. (a) A schematic illustration of programming the direction of asymmetric ratchet structures by a modified Lucius prism array. (b) The control of liquid flow velocity by the ratchet orientation along with representative movie cuts. The graph demonstrates the change in liquid flow velocity on the programmed asymmetric structures. (Insets: a schematic of asymmetry of ratchets of different regions and microscopic pictures of interfaces)

films to alter the light direction (also, see Supporting Information S2). In the present study, we prepared a *Lucius* prism array to tilt incident light to the right direction in the areas A and C while bending light path to the left direction in the area B. We then exposed UV light after filling liquid prepolymers within the channel followed by the removal of unreacted prepolymers. To demonstrate the change in liquid flow speed on the programmed structural array, we discharged liquid (water colored in red) from the left end of the microchannel, as shown in the movie cuts in Figure 3b. As shown in the graph of the liquid front position as a function of time (Figure 3b), we could easily vary the fluid speed in a particular region within a channel by simply changing the orientation of a ratchet structure. In the regions A and C, the average velocities of liquid flow are about ~13.9 μm/s and ~14.6 μm/s, respectively while the flow velocity increases to ~47.4 μm/s in the region B. The difference in the flow speed is due to the difference in the net forces on different contacting surfaces, which is, in turn, dependent on the base angles of asymmetric ratchet structures created within the channel.[21,24,27–29] The results shown in the present study clearly lay a firm foundation to control the flow speed within microchannels simply by changing the direction of asymmetric ratchet orientation.

The second demonstration of the direct realization of ratchet structures with different orientations is a microchannel of three pathways with different timings of fluid flow. For time-dependent assays including immunoassays or enzymatic reactions, delayed fluid flow could be effectively used in the aspect of time-dependent fluid injection.[17,30,31] To demonstrate the delayed fluid flow, a fluid (water mixed with red dyes in this case) was injected into three pathways with different asymmetric structures within a channel, as shown in **Figure 4**. To conduct experiments for the delayed fluid flow, a microchannel with three pathways was prepared through the conventional photolithography process. To realize three different asymmetric structures in different microchannel pathways of regions 1 to 3, we designed a *Lucius* prism array with programmed ratchet directions in three different pathways. In the region 1 (Figure 4), the guided transmission of light realized the asymmetic ratchets to the direction of smaller resistance. Also, the asymmetric ratchets in the reverse direction (region 3) and symmetric ratchets (region 2, w/o a Lucius prism array) were formed at the same time. Three different pathways with three different ratchet orientation angles, realized within a microchannel, demonstrate the controlled fluid wicking behavior. We observed the first fluid flow to region 1, followed by the flow into region 2 with symmetric ratchets with a time delay of 50 s. After reaching the regions 1 and 2, the fluid flow finally switched to the region 3 with the highest resistant force with a time delay of 100 s, as shown in Figure 4. The delayed fluid flow in a programmed microchannel system could be useful in comparison with the previous trials employing surface treatment approaches[17,30] in terms of facile and economic fabrication of microchannels.

In this paper, we present a simple but powerful strategy to directly realize or program asymmetric structures within a microchannel by a combination of photopolymerization within a microchannel and the guided light transmission through an optically asymmetric *Lucius* prism array. We took advantage of the selective light refraction into one direction through

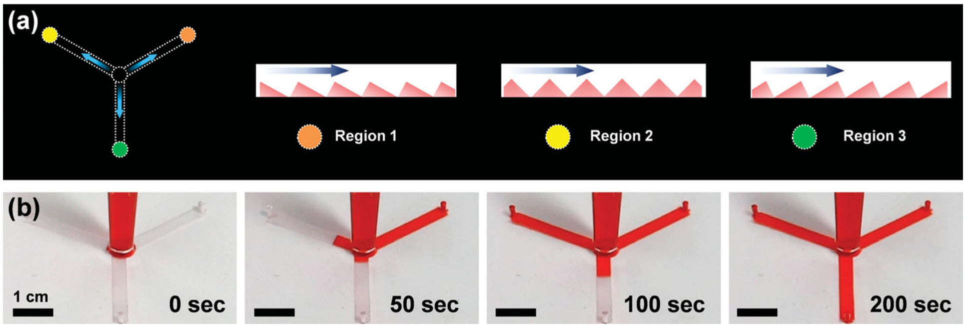

Figure 4. An example showing the delayed fluid flow based on different ratchet structures created within a microchannel. (a) A schematic illustration on differently oriented ratchet structures in three different channel regions. (b) Movie cuts showing the delayed fluid flow induced by different ratchet structures. In good agreement with the previous experimental results of controlled liquid flow velocity, injected liquid sequentially reached the regions 1, 2, and 3 with time lapse.

the optical *Lucius* prism array to crosslink liquid prepolymers within a channel, yielding asymmetric ratchet structures. The asymmetric ratchet structures, created at the bottoms of microchannels, show the unidirectional liquid flows as well as controlling the fluid speed in a predefined region. Furthermore, we demonstrated two examples of asymmetric structures created or programmed in specific regions within microchannels to control the fluid speed in predefined regions and to be used as on-chip timers in split microchannels.

Experimental Section

Fabrication of the a Lucius Prism Array: In this paper, we used the *Lucius* prism array with 50 μm in period and 45° in prism angle.[7,13] After the preparation of the polymeric prism array by the replica molding, we deposited ~100 nm thick Cr metal films on one faces of the prism array using an oblique metal evaporation. We used a E-gun evaporator (V-system) for the metal deposition and placed the polymer prism array on an inclined holder with an angle 60°. The detail procedure of the fabrication can be found elsewhere.[7,13]

Fabrication of Asymmetric Ratchet Structure in Microfluidic System: Microfluidic channel (3 mm in width, 200 μm in height) composed of polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning) was prepared with the mixing ratio of 10:1 (prepolymer: curing agent) and curing temperature of 60 °C for 2 h. Then, the PDMS channel punched with two holes for inlet and outlet of fluid was bonded onto a glass sheet (150 μm of thickness). For the fabrication of asymmetric ratchet structure in microfluidic channel directly, ultraviolet (UV)-curable polyurethaneacyrlate (PUA) prepolymer was filled into the channel and photomask of line shape with a width of 40 μm and a space of 40 μm and the Lucius prism array was arranged onto the backside of glass substrate layer by layer. Then, vertical UV exposure (400 mJ/cm^2, 365 nm in wavelength) to the Lucius prism array for 10 s induced crosslinking of prepolymer in microchannel resulting in an asymmetric ratchet structure. The unreacted prepolymer was rinsed with DI water several times and fabricated structures was dried in a dry oven for more than 4 h.

Measurements: SEM images were taken using FESEM (Hitachi S-48000, Japan). Liquid flow movie cuts were obtained by a digital video camera (SONY DSC-T30, Japan).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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