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One step fabrication of polymeric ratchet structures of diverse tilting angles†

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Asymmetric micro/nano structures in nature provide diverse multifunctional properties including directional water transport, light transmission and adhesion. Due to these intriguing features, the fabrication of an anisotropic surface has been extensively studied as a broad research area. Herein, we present a novel strategy to fabricate asymmetric ratchet-like polymeric structures with various tilting angles by using photo-polymerization and controlling light refraction. We used a prism array that allows directional light transmission through the refraction on one face of it. To construct symmetric ratchets by negating the refraction effect in a specific area, we filled the region of the array with a refractive index matching liquid. To make a ratchet structure with a higher tilting angle, we used two films of the designed prism arrays to refract twice. Furthermore, we demonstrate one step fabrication of ratchet structures with tilting angles of 0°, 24.4° and 49.7° through the combination of the refractive index matching method and double-refraction on two layers of prism arrays.

1. Introduction

There are diverse asymmetric surface morphologies of living things in nature that provide directional adhesive, wetting, and optical properties.[1–5] For example, a morpho-butterfly repels water droplets on their wings with their asymmetric structures.[6,7] A gecko lizard climbs on any wall surface with a very high degree of adhesion hysteresis (*i.e.*, strong attachment and easy detachment).[8–11] These directional properties come from the asymmetric micro/nano structures of the surface of their body.

To apply these properties into engineering research and industrial fields,[12,13] various fabrication methods have been extensively studied, including oblique angle polymerization (OAP),[14] angled etching technique in Faraday cage,[8] oblique metal deposition,[15,16] and partial UV-exposure method.[17] Recently, a fabrication method of asymmetric ratchet structures within micro-channels through directionally-guided light transmission with designed prism arrays was reported.[18] The Lucius prism arrays with one face deposited with metal films to block the light penetration can refract the incident light and guide its pathway to a specific direction. When we combine the directional transmission from the arrays and photo-polymerization of UV-curable prepolymer coated on a mask, we obtain asymmetric tilted ratchet structures. Although the method is advantageous in the aspect of direct polymerization without using the patterned silicon master and the demolding process, there are limitations to building ratchet structures with high tilting angles. In order to fabricate high-tilted structures, the refractive index of prism arrays and their angles should be controlled. In addition, it is important to form a diverse, position-dependent asymmetric structure with different tilting angles in one substrate for potential applications such as in microfluidics. However, it is difficult to synthesize high refractive index polymers and expensive to fabricate a master mold with different prism angles.

Herein, we propose a novel method to manipulate tilting angles of ratchet structures without changing the angle or refractive index of prism arrays. To negate the refraction effect in a specific region, we use a method of filling refractive matching liquid in the prism area. Also, we make the ratchet arrays with a higher tilting angle by using two layers of the Lucius prism array. The tilting angle with two layers could be calculated by Snell's law and the experimental data is in accordance with the model. Furthermore, we demonstrate the one-step fabrication of diverse micro structures with different tilting angles in one substrate by combining the refractive index match and the double refraction through the prism arrays.

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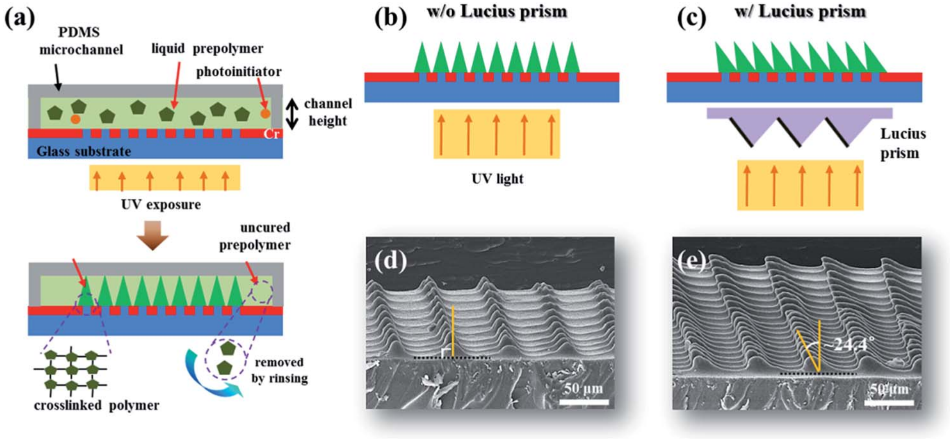

Fig. 1 (a) Schematic illustrations of the principle of backside UV-assisted photopolymerization using liquid prepolymer mixed with photoinitiator. (b and c) Fabrication of ratchet arrays with and without Lucius prism array. (d and e) Corresponding SEM images of symmetric and asymmetric ratchet structures.

2. Experimental

First, we prepared prism arrays with 50 μm in period and 45° in prism angle by mechanical machining. Next, the transparent polymeric prism arrays with the material of PUA (MINS 301, Minuta tech.) were replicated from the master.[19–21] To coat metal films on one faces of each prism, we placed the prism arrays on an inclined holder with the angle of ~45° and deposited Cr films with ~100 nm in thickness by using oblique metal evaporation with E-gun evaporator (V-system). The detailed procedure of the fabrication was introduced in the previous studies.[16,22]

Fig. 1(a) shows the schematic illustration of the fabrication of ratchet arrays by photopolymerization. After preparing polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning) microchannel (4 mm in width, 300 μm in height), we filled the channel with liquid prepolymer mixed with photoinitiator. In the experiments, we used functionalized UV-curable polyurethaneacyrlate (PUA) prepolymers mixed with photoinitiators (MINS 301, Minuta tech). On the substrate, chromium microholes with a diameter of 40 μm and the space of 40 μm were fabricated by conventional photolithography as well as wet etching process. The Cr holes play a role of a photomask in the backside UV-assisted photopolymerization. When the mixture was exposed to the UV light, free radicals are generated in the photoinitiators, which induced the photopolymerization of PUA. After the crosslinking to fabricate symmetric or asymmetric ratchet arrays as shown in Fig. 1(a), the remaining unreacted prepolymers in the microfluidic channel were rinsed away with solvent several times and then dried. The polymerization of PUA in the PDMS micro-channel could be partially prohibited by oxygen inhibition through the permeable PDMS channel (Fig. S1†). As a post UV exposure, the fabricated ratchet arrays were exposed by UV light in the same condition for more than 10 hours to ensure full crosslinking.[19]

Fig. 1(b) and (e) demonstrates the results of symmetric and asymmetric ratchet structures fabricated on glass substrates. After the vertical UV light (400 mJ cm^{-2}, 365 nm in wavelength) was exposed to the glass substrate with Cr mask for ten seconds, crosslinked PUA displays a symmetric ratchet structure on the glass substrate (Fig. 1(b) and (d)). When we inserted the Lucius prism arrays between the glass substrate and the UV light, we obtained the asymmetric ratchet structures on the glass substrate (Fig. 1(c) and (e)). This is due to the fact that the UV light through the Lucius prism arrays cannot penetrate the metal surface. It can only pass through the transparent polymeric face and is refracted with an angle predicted by the Snell's law. The height of the ratchets could be modulated with the exposure time as well as the thickness of liquid prepolymer defined by the height of the PDMS microchannel.

3. Results and discussion

The incident light changes its pathway when it reaches the interface of two different materials with different refractive indexes. In our case, as the illuminated UV light passes through the prism structure, it changes its pathway and is refracted by Snell's law[16] as follows:

$$\frac{\sin\theta_i}{\sin\theta_j}=\frac{n_j}{n_i}, \qquad (1)$$

where n_i is refractive index for ith material, and θ_i is the angle of the light pathway in the i_th material. To control the light pathway, we dispensed refractive index matching liquid (*i.e.* PUA prepolymer, glycerol) onto the prism arrays. At first, the dispensed liquid filled the gap of prism structures in the line direction of the arrays. Then, the liquid flow showed a step-wise movement with a stick-slip behavior and the droplet filled the entire micro-prism arrays as previously reported.[15,21,22] As a result, the final shape of the liquid-filled region was a transparent rectangle as shown in Fig. 2(a). In addition, the liquid-filled region was flattened as shown in the red-squared box of Fig. 2(b), because the liquid material is completely wetting the micro-prism along the parallel direction with grooves on the

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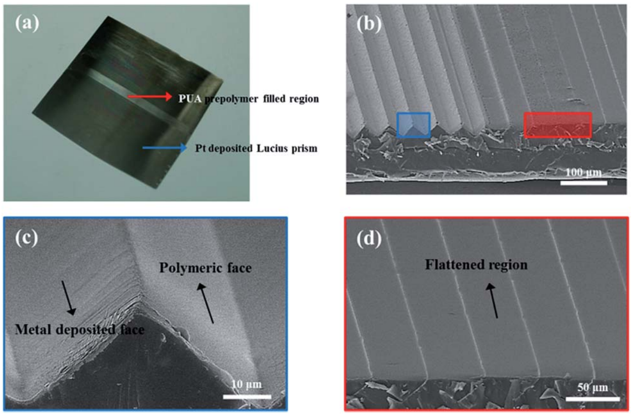

Fig. 2 (a) A digital camera image of the prism arrays regionally filled with liquid to control the local light pathway. (b–d) Corresponding SEM images of locally PUA prepolymer filled Lucius prism arrays.

PUA surface. The magnified SEM images of blue and red-squared boxes in Fig. 2(b) show the original micro-prism structure with one-side metal deposited face (Fig. 2(c), blue-square) and the flattened region filled with liquid (Fig. 2(d), red-square), respectively. When the light passes through the flattened area, the liquid-filled region, it would not change its pathway. This means that we can locally negate the refraction effect through prism arrays and control its local pathway by filling the prism arrays with the regional refractive matching liquid.

In addition to the strategy to remove the refraction effect on the prism array, we also propose a method to refract the incident light above the limitation expected of the single-layered prism array. As previously described, single-layered Lucius prism arrays allow directional transmission of light with a specific angle. However, it is hard to bend the light pathway more than the specific angle because the modification of the prism structure is difficult due to the limitation of machining process that requires high cost and long process time.[16] Also, it is one of the obstacles to synthesizing transparent polymers with high refractive index. To address this issue, we overlapped and arranged two of the same films of Lucius prism arrays. Then, the light pathway can be bent twice as it passes through the two layers of prism structures. Following the same method to fabricate asymmetric ratchet structures on the glass substrate as previously mentioned, we obtained the highly tilted asymmetric ratchet structures by using the double-layered Lucius prism arrays and UV light illumination to the PUA prepolymer as shown in Fig. 3(a) and (b).

To investigate the control of the light pathway by the regional liquid filling of the Lucius prism arrays and the double-layered arrays, we proposed simple modeling as shown in Fig. 3(c) which is the schematic illustration of light transmission pathway. If the light penetrates one layer of prism films, it would refract by θ_3. And this angle can be expressed as the following equation,

$$\theta_3 = \sin^{-1}\left(\frac{n_2}{n_3}\sin\left(\alpha - \sin^{-1}\left(\frac{n_1}{n_2}\sin\,\theta_1\right)\right)\right), \tag{2}$$

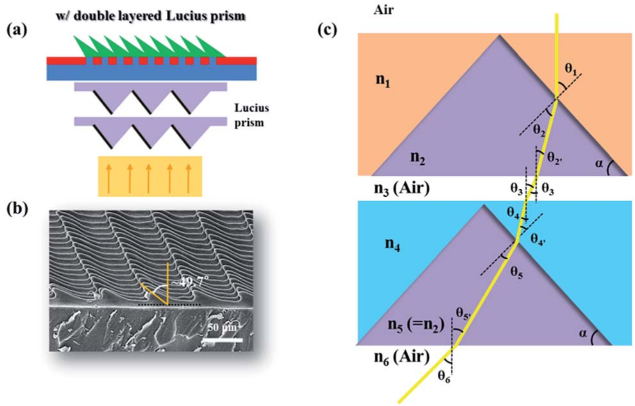

Fig. 3 (a) Schematic illustrations to show the control of light pathway by using the double-layered Lucius prism array. (b) Corresponding SEM images of asymmetric ratchet structure by using the double-layered Lucius prism array. (c) Schematic illustration of the light transmission pathway *via* liquid-filled double-layered Lucius prism array.

where n_i is refractive index for i_{th} material, and α is the ridge angle of prism structure. If there is no liquid material on the prism film, n_1 is refractive index for air. And the value of θ_3 is calculated as ~24.4°, which is in good agreement with the experimental result in Fig. 1(d). However, if the specific liquid material (in our case, we used the prepolymer of PUA; see Table 1) fills the prism structure, the value of θ_3 is calculated as ~0°, because the refractive indexes are the same ($n_1 = n_2 = 1.473$). This means that the refraction of the prism structures would be reduced on the flattened region due to the liquid-filled prism array. In the same way, if we use the double-layered Lucius prism arrays, we can adjust the light pathway to be more slanted as the following equation.

$$\theta_6 = \sin^{-1}\frac{n_5}{n_6}\sin\left(\alpha - \sin^{-1}\left(\frac{n_4}{n_5}\sin\left(\alpha - \sin^{-1}\left(\frac{n_3}{n_4}\sin\,\theta_3\right)\right)\right)\right) \tag{3}$$

When the prism structures are not filled with any liquid, the θ_6 is calculated as ~49.7° (Fig. 3(b)), which is a high value without any modification of the prism structure. In the case where the two films of prism structures are filled with the prepolymer of PUA, θ_6 is also calculated as ~0°. This means that we can regionally adjust the angle of light transmission pathway by filling the polymeric prism arrays with liquid.

Based on the results, we have designed the angle of light pathway locally, and achieved one step formation of diverse asymmetric ratchet structures on one glass substrate. We

Table 1 Refractive index (n) for diverse materials at $\lambda = 365$ nm

Air	1.000
Water	1.333
Ethanol	1.360
Glycerol	1.473
PUA	1.473

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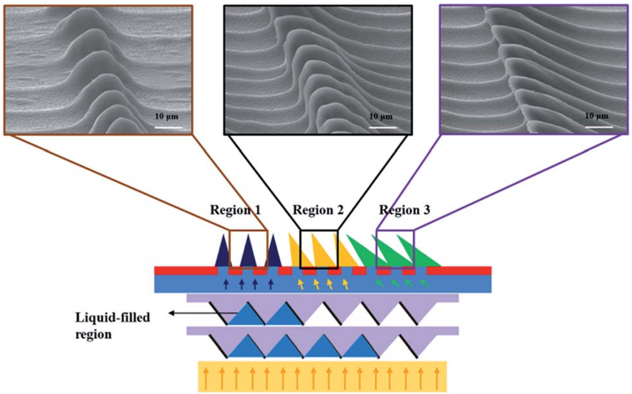

Fig. 4 One step formation of diverse ratchet-like micro structures through the combination of the regional control of liquid-filled Lucius prism arrays and stacking their layers.

prepared two films of Lucius prism arrays which were locally filled with PUA prepolymer as shown in Fig. 4. After arranging the films, we illuminated UV light on them. As a result, we obtained ratchet structures with different tilting angles on the regions 1, 2 and 3. In the region 1, the prism effect for the transmitted light was reduced by the liquid-filled prism structures, which leads to the construction of symmetric ratchet structures. And, as previously analyzed, the transmitted UV light with the angle of ~24.4° in the region 2 and ~49.7° in the region 3 induced locally different asymmetric ratchet structures.

4. Conclusions

In this paper, we have presented a facile strategy to fabricate asymmetric structures through the combination of regional control of liquid-filled Lucius prism arrays and stacking of the layers with the aid of backside UV-assisted polymerization of UV curable materials. With this method, we have guided and controlled the light transmission through optically asymmetric Lucius prism array. We utilized the selective light refraction of the optical Lucius prism arrays for the crosslinking of liquid prepolymers within a microfluidic channel, creating locally different asymmetric ratchet structures in the predefined regions. The locally controllable asymmetric structures would be applicable to generation of different flow velocities in microfluidic systems or controllable anisotropic adhesive systems.

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