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Integration of Great Water Repellence and Imaging Performance on a Superhydrophobic PDMS Microlens Array by Femtosecond Laser Microfabrication

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Microlens arrays (MLAs), as the important optical devices, are easily polluted by the water droplets or power-like-contaminates in the air. Endowing the artificial MLAs with anti-water and self-cleaning abilities remains great challenge. In this paper, the authors report a novel method for fabricating superhydrophobic polydimethylsiloxane (PDMS) MLAs by the combination of femtosecond laser wet etching and femtosecond laser direct writing methods. The resultant surface is composed of a convex MLA and the surrounding rough micro/nanoscale hierarchical structures. Water droplet on the surface of the as-prepared MLA shows a contact angle of 162° and can easily roll away when the substrate is slightly tilted 0.5°. In addition to their excellent imaging performance, such ultralow adhesive and ultrahigh superhydrophobicity also endows the as-prepared MLA with excellent anti-water ability as well as the self-cleaning function relative to the normal MLA. The authors believe that the anti-water and self-cleaning MLAs will potentially have many important applications in solar cells, medical endoscopes, and other optical systems that are often used in the humid environment or outdoors.

1. Introduction

Microlens arrays (MLAs), serving as crucial optical elements, are widely used in various micro-optical systems, such as fiber coupling,[1] artificial compound eyes,[2,3] solar cells,[4,5] biochemical observation, and detection,[6,7] because of their small size, high integration, and excellent optical capability. However, the wide applications of MLAs are still restricted by some limitations. For instance, many microlenses or MLAs work in an easily polluted environment, such as the humid or outside air. Accumulation of water droplets (such as rain droplets and dew) and dusts on the surfaces of these optical devices can seriously weaken their optical performance. Frequent cleaning those pollutions by the lens wiping paper may damage the surface of the fine optical instruments and lead to a decrease of their lifetime. Furthermore, the optical system must be dismantled to remove the adhered water droplets or dusts on the surface of the microlens-based elements in some cases. The delay during the repair will cause large economic losses. From a practical point of view, the fabrication of the MLAs that have remarkable self-cleaning and waterproof properties is highly desired.

Many natural plant leaves have evolved optimal surface microstructures with waterproof property.[8,9] Lotus leaf is one of the most well-known and studied superhydrophobic plant.[10,11] Superhydrophobicity allows water droplets to easily roll off the lotus leaf and take the dusts on the surface away, ensuring the lotus leaf always keep clean. Such ability is generally called "self-cleaning effect" or "lotus leaf effect".[12] The surface of lotus leaf is found to be covered with a large number of micro/nanoscale hierarchical papillae and a layer of low-surface-energy wax crystal.[12,13] The superhydrophobicity is indeed ascribed to the synergy between the rough surface microstructure and the hydrophobic chemistry.[14] Inspired by lotus leaf, building micro/nanostructures or even hierarchical rough structures on a low-surface-energy substrate becomes an effective way to achieve superhydrophobicity.[15–21] For instance, Im and his co-workers prepared superhydrophobic polydimethylsiloxane (PDMS) surface with uniformly ordered inverse-trapezoidal microstructures based on the lithography technique and a double replication process.[22] Bhushan and his co-workers fabricated self-cleaning functional surfaces with micro/nanoscale hierarchical structures by replicating a micropatterned silicon surface and self-assembly coating with hydrophobic alkanes.[23] Recently, femtosecond laser ablation is considered to be an effective way to fabricate superhydrophobic surfaces because the femtosecond laser can

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DOI: 10.1002/adem.201800994

not only process a variety of materials but also directly induce various hierarchical rough microstructures.[24–26] By controlling the computer program, complex structures can be obtained to realize unique wetting property.[27,28] Zhang and his co-workers reported a superhydrophobic surface via irradiating silicon substrate by a femtosecond laser and subsequently coating with fluoroalkylsilane monolayer to lower the surface free energy.[29] Fang and his co-workers fabricated superhydrophobic microstructures on the polytetrafluoroethylene (PTFE) substrate by a femtosecond laser. To obtain superhydrophobicity, the surface of the materials should have appropriate micro/nanoscale rough structures.[30] In contrast, the surface of traditional microlenses and MLAs must be smooth enough to ensure their basic imaging capability. Therefore, the integration of great imaging performance and water repellence as well as the self-cleaning function by fabricating a novel superhydrophobic MLAs is still urgent and remains a big challenge.

In this paper, we fabricated a superhydrophobic PDMS MLAs by combing two different kinds of femtosecond laser treatments. The resultant surface mainly contains a convex MLA and the rest surrounding rough area. The MLAs that formed by femtosecond laser wet etching (FLWE) and further template replication enable the samples possess good imaging capability. The rest rough area surrounding every microlens is generated by the subsequent femtosecond laser direct writing process, which results in superhydrophobicity of the as-prepared MLAs. Water droplets can easily roll away on the surface of the as-prepared MLAs, revealing strong repellence between droplets and the laser-structured samples. Additional measurements demonstrate that the sample also possesses excellent self-cleaning ability besides its inherent perfect optical performance.

2. Results and Discussion

2.1. Fabrication of MLA-Textured Surfaces

The fabrication process can be divided into three steps: fabrication of concave MLA-structured template, convex MLA, and femtosecond laser-induced microstructures. The details are summarized in the Experimental Section. The concave MLA was generated on the glass surface through FLWE technology, as reported in our previous works.[31,32] The FLWE mainly includes two steps: femtosecond laser ablation and chemical wet etching. To obtain a convex MLA on the PDMS surface, the concave MLA-structured glass sheet was used as a template and the template-replicated method was implemented. The hierarchical rough microstructures were easily created by line-by-line scanning manner on the rest flat area (**Figure 1**a). Figure 1b shows the top view of the fabricated as-prepared MLA. The scanning speed and the interval of adjacent scanning lines were set at 4 mm s^{-1} and 4 μm, respectively. There are two crucial geometrical parameters: the central distance (D) of the two adjacent microlenses and the width (W) of the laser-scanned region.

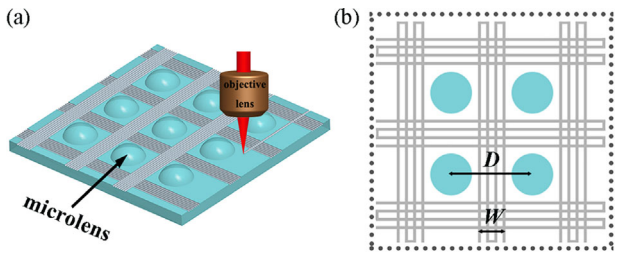

Figure 1. a) Schematic illustration of the fabrication of criss-cross reticular rough structures around the microlenses. b) Top view of the as-prepared MLA.

2.2. Morphology of the As-Prepared PDMS MLAs

Figure 2a and b show the SEM images of the as-prepared PDMS surface ($W = 92$ μm), which was consisted of a convex MLA and rest femtosecond laser-induced rough area. Microlenses were uniformly arranged on the non-ablated square area, and each microlens was surrounded by the femtosecond laser irradiated domain (Figure 2a). There is an obvious boundary between the non-ablated square and the surrounding laser-treated domain. Inset of Figure 2a represents a single microlens. The microlens has a spherical shape and a very smooth surface which is important to its imaging capability. Figure 2b illustrates the large magnified image of the laser-induced rest rough area between the microlenses, which is characterized by an irregular rough microstructure decorating with hundreds of nanoscale lumps. It has been demonstrated that forming micro/nanoscale hierarchical structures on PDMS surface is an efficient way to endow PDMS surface with superhydrophobicity.

The 3D profile and cross section of the convex microlens were investigate by the laser confocal scanning microscope, as shown in Figure 2c and d. The measured result shows that the diameter (d) and the height (h) of the convex microlens are 49.96 μm and 7.46 μm, respectively. The focal length (f) and numerical aperture (NA)of the convex microlens can be calculated by the following equations[33]:

$$f = \frac{r^2 + h^2}{2h(n\text{-}1)} \tag{1}$$

$$NA = D/2f \tag{2}$$

where r is the radius of the microlens ($r = d/2$), and n is the refractive index of the material ($n = 1.406$ for PDMS). Given $d = 49.96$ μm, $h = 7.46$ μm, the f and NA can be calculated as 112.20 μm and 0.22, respectively.

2.3. Wettability of the Resultant MLAs

Figure 3 shows the water wettability of the as-prepared MLA, compared to the normal MLA without laser-induced rough microstructures around each microlens. When a water droplet was put on the as-prepared surface, the droplet could maintain a spherical shape with a CA of 161.5 ± 1° (Figure 3a). As long as the sample was tilted about 0.5°, the droplet could easily roll away (Figure 3c). The results demonstrate that the resultant MLA surface shows both superhydrophobicity and very low adhesion

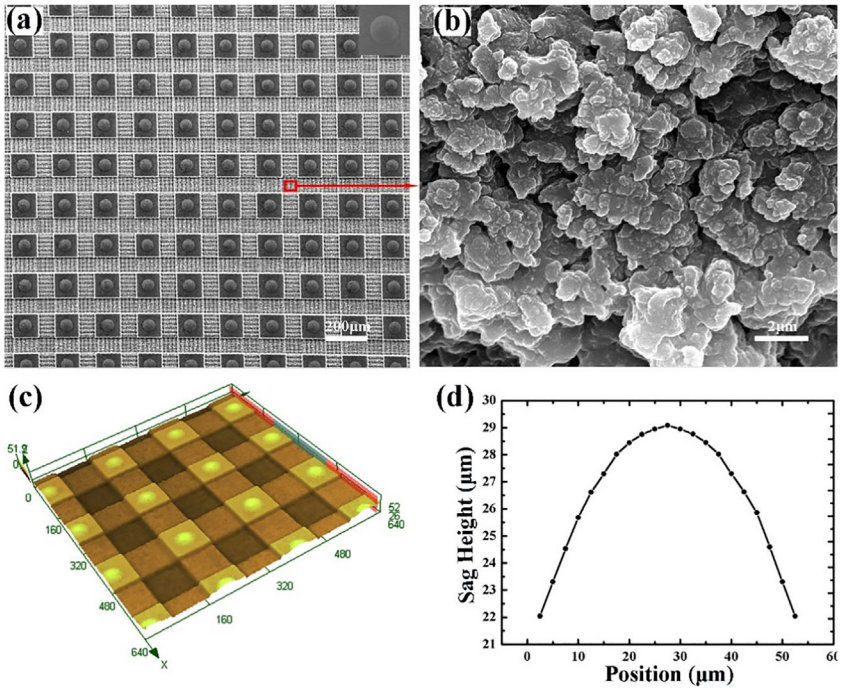

Figure 2. The morphology of the as-prepared MLA. a) SEM images of the as-prepared PDMS MLA (inset represents a single microlens). b) Large-magnified image of the laser-induced microstructure. c) 3D morphology of the fabricated sample. d) The cross-sectional profile of the fabricated microlens.

to water droplets. However, if the surrounding area of every microlens is not ablated by femtosecond laser thereby does not have hierarchical rough microstructure, such MLA only exhibits ordinary hydrophobicity with the CA of $101.5 \pm 1°$ to a water droplet (Figure 3b). Water droplets are very inclined to adhere to the surface of the normal MLA.

Femtosecond laser ablation resulted in the formation of micro/nanoscale rough structures on the irradiated PDMS domain. It has been demonstrated that surface roughness has the ability to amplify the nature of the wettability of a solid substrate. When a water droplet was placed on the laser-induced PDMS microstructure, air could be trapped in the rough surface

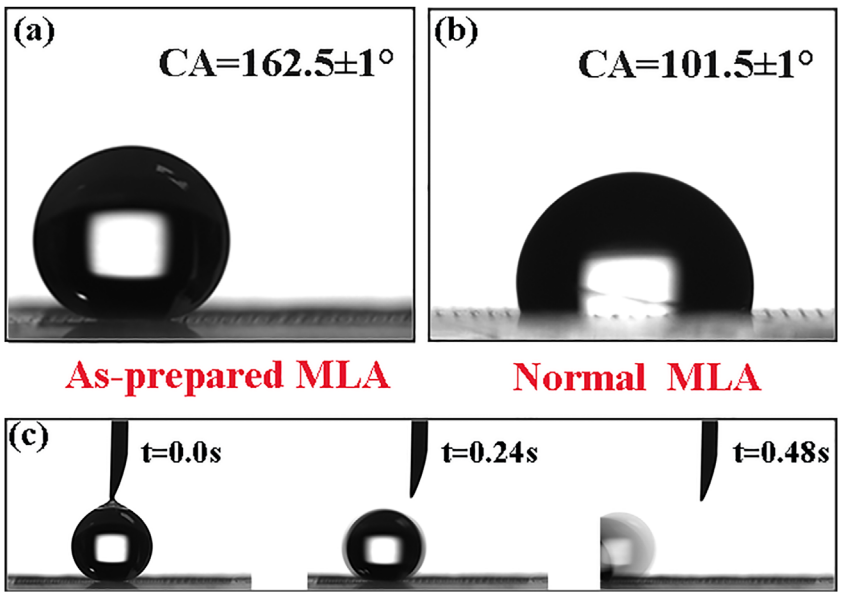

Figure 3. Wettability of the as-prepared samples. Shapes of a water droplet on the: a) as-prepared MLA and b) normal MLA without rough microstructures. c) Time sequence of snapshots of a water droplet rolling on the 0.5° tilted as-prepared MLA surface.

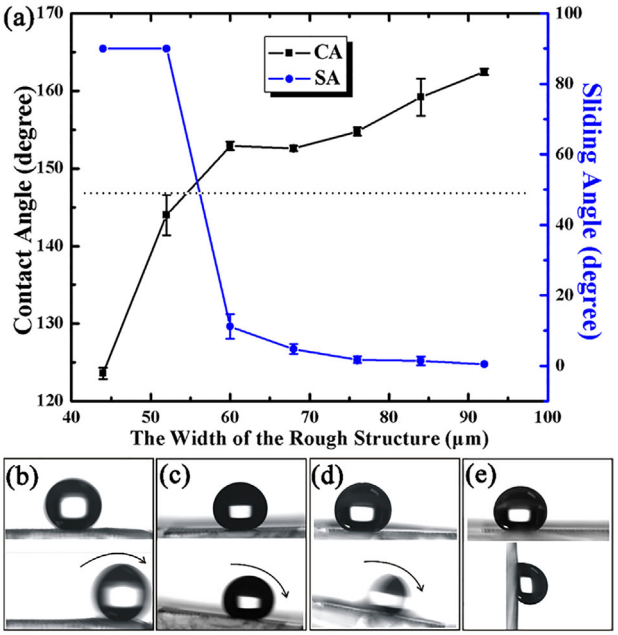

Figure 4. a) The relationship between the W of the laser-induced rough structures and the CA (left)/SA (right). b–e) Static properties and the dynamic behaviors of water droplets on the as-prepared PDMS MLAs with different W: b) $W = 92\ \mu m$, c) $W = 76\ \mu m$, d) $W = 60\ \mu m$, and e) $W = 52\ \mu m$. The arrow in the b–e) indicated the rolling direction of water droplets on the as-prepared surfaces.

microstructure and the trapped air cushion would form underneath the water droplet. Such water droplet was at the Cassie wetting state.[34] The air cushion prevented the droplet from effectively touching the PDMS surface, allowing the droplet to only contact with the top of the rough microstructure. Therefore, the femtosecond laser ablated PDMS surface showed superhydrophobicity and low adhesion to water droplets. Although the surface of the MLA was very smooth, the microlens domain was enough smaller than the surrounding laser-induced rough domain. As a whole, the resultant MLA synthetically exhibited ultralow adhesive superhydrophobicity.

The W is the most crucial structure parameter, which has an important effect on the CA and SA of the as-prepared MLA surfaces. **Figure 4**a shows the relationship between the static CA and the dynamic SA with W on the as-prepared surfaces. When W was larger than 60 μm, the as-prepared surfaces showed superhydrophobicity with the CA larger than 150° and ultralow adhesion with the SA smaller than 10°. Figure 4b–d show the shape of a water droplet on the PDMS MLAs with different parameters of W. The CAs were $162.1 \pm 0.5°$ ($W = 92\ \mu m$), $154.7 \pm 1°$ ($W = 76\ \mu m$), $152.2 \pm 1°$ ($W = 60\ \mu m$), and $148.2 \pm 0.9°$ ($W = 52\ \mu m$), respectively. The hydrophobicity of the as-prepared MLA with W of 44 μm was very similar to that of PDMS. In the aspect of the SA of the as-prepared MLAs, the SA increased gradually with the decrease of the W. When the W was in the range from 60 to 92 μm, the water droplet could roll down

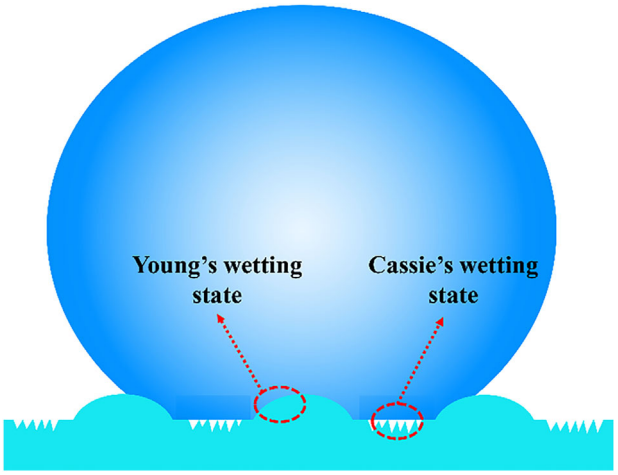

Figure 5. Contact model of the water droplet on the as-prepared MLA surface consisting of micro/nanoscale rough structures and non-irradiated region.

easily when the surface was tilted at a small angle below 10°, or even shaken slightly (Figure 4b–d). However, with the value of W decreased from 60 to 52 μm, the SAs on the surface of the as-prepared MLAs sharply increased from 10° to 90° that the droplet doesn't slide down even though the surface turned vertical (Figure 4e). Finally, the droplet was firmly pined on the as-prepared surfaces without any movement at any tilted angles when W was smaller than 44 μm.

The laser-structured rough PDMS surface shows superhydrophobicity and ultralow water adhesion, revealing that the water droplet on the laser-structured area is at the Cassie wetting state. The water droplet contacts the PDMS surface only through the top of the asperities. On the contrary, water droplet is able to completely wet the non-irradiated domain consisting of flat surface and microlenses, belong to the Young's wetting state.[35] As a result, the non-irradiated region shows ordinary hydrophobicity and ultrahigh adhesion because the large contact area lead to more van der Waals force. In this experiment, the as-fabricated MLAs consists of laser-induced micro/nanostructured region and smooth non-irradiated region. Therefore, a water droplet on the as-prepared MLA surface is a composite contact model which consist of the Cassie's wetting state and Young's wetting state, as shown in **Figure 5**. With the increase of W, the area fraction of the laser-induced rough microstructure as well as the Cassie wetting domain increase, resulting in the enhancement of the surface hydrophobicity and the decrease of the water adhesion for the resultant MLA surface. It is found that the as-prepared PDMS MLAs show superhydrophobicity and ultralow adhesion when the W is larger than 60 μm. Based on this result, we calculated the area fraction of the femtosecond laser-induced rough domain and the value was 54%. Therefore, the superhydrophobic and low adhesion MLA can be obtained as long as the area fraction of the micro/nanostructured domain is larger than 54%.

2.4. Anti-Water and Self-Cleaning Ability

The anti-water property of the as-prepared superhydrophobic MLAs was tested, compared to that of the normal MLAs. **Figure 6**a shows the optical image of a horizontal PDMS sheet where both the superhydrophobic MLAs domain and the normal MLAs domain on its surface. When a jet of water (blue color) was sprayed onto the whole sample surface randomly, water was able to adhere to the domain with normal MLAs, while there was no water residual on the domain with superhydrophobic MLAs (Figure 6b and Supporting Information 1). The result revealed that the as-prepared superhydrophobic MLA had strong water repellence. Due to the superhydrophobicity and ultralow adhesion we have mentioned above, the as-prepared MLAs possess excellent self-cleaning ability. When a water droplet was dripped onto the surface of the as-prepared superhydrophobic MLA that was previously polluted by chalk powders and was tilted at a small angle, water droplet would roll off easily on the

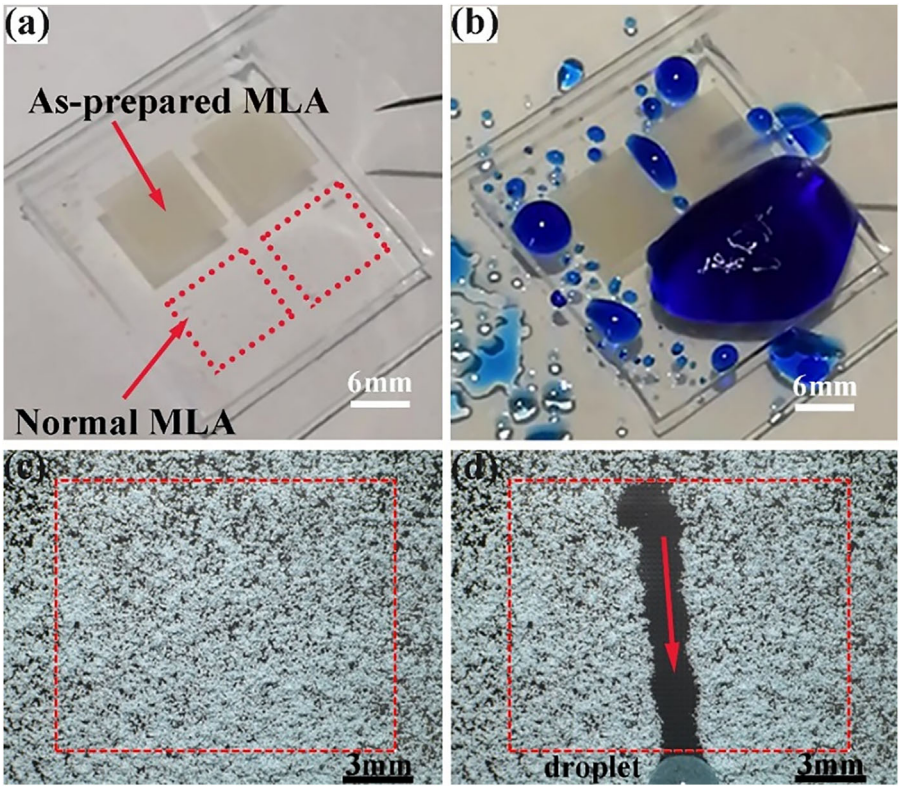

Figure 6. a) Photography of a PDMS surface composed of both the superhydrophobic MLAs domain and the normal MLAs domain. b) Spraying a jet of water (blue color) onto the whole sample surface randomly. c) Photography of a polluted sample. d) Photography of the polluted surface after water droplet rolling away.

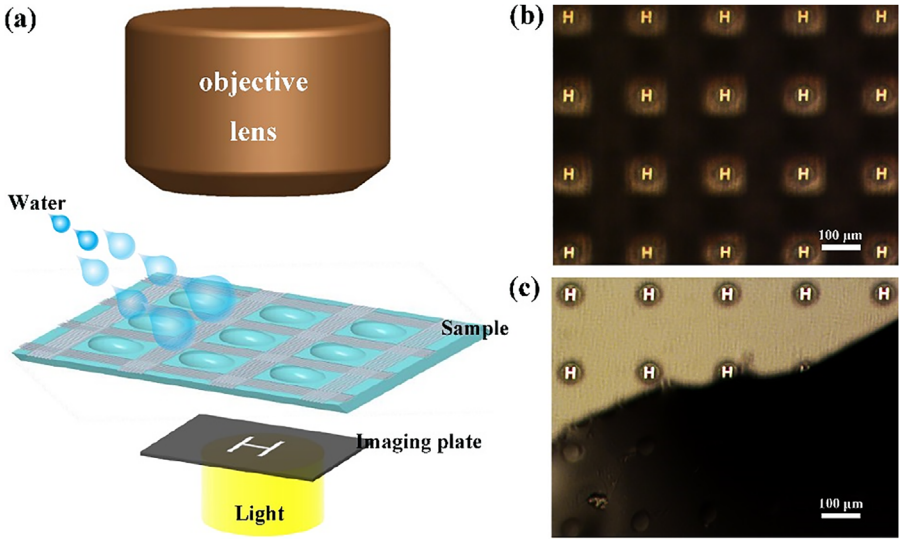

Figure 7. Optical imaging performance of the as-prepared superhydrophobic MLA compared to the non-irradiated smooth MLA. a) The schematic illustration of the optical observation system. b,c) Imaging results of the water-polluted MLA: b) superhydrophobic MLA, and c) normal MLA domain.

sample surface and took the contaminants on their path away (Supporting Information 2). The polluted surface looks very messy (Figure 6c), whereas the area where the droplet has rolled away is clean without any pollutant residuals (Figure 6d).

2.5. Optical Performances

As one of the basic performances of MLA, the imaging capability of the resultant MLA was investigated by the optical observation system (**Figure 7**a). The water droplet was dripped onto the whole sample surface to simulate the applications scenarios. It could be found that the adhesion of water droplets could seriously weaken the imaging result of the normal MLA (Figure 7c). There were almost no recognizable images in the area where was wetted by water (black area in the optical image). In contrast, uniform and clear images of "H" could be captured by the superhydrophobic MLA (Figure 7b). The excellent imaging capability of the superhydrophobic MLA was not influenced by the water droplets because water is not able to stick on the MLA.

The imaging performance of the spot light source was also tested by using an optical microscope. When light was incident onto the focal plane of the as-prepared MLA, each microlens produced a focal spot (**Figure 8**a). To quantify the optical focusing, the cross-sectional intensity distribution of the focal spots in the selected rectangular area was calculated and shown in Figure 8b. The intensity distribution curve of each foal spot was quite uniform and corresponded with Gauss distribution. Figure 8c shows the 3D intensity distribution of the focal spots. These results demonstrate that the as-prepared MLA perform good consistence of focal length and a well focusing ability.

3. Conclusions

In summary, superhydrophobic PDMS MLAs with anti-water and self-cleaning properties were fabricated by femtosecond laser wet etching and subsequent femtosecond laser direct writing. By the ingenious combination of the smooth convex MLA and the rest surrounding laser-induced rough micro-structures, both excellent optical imaging capability and anti-

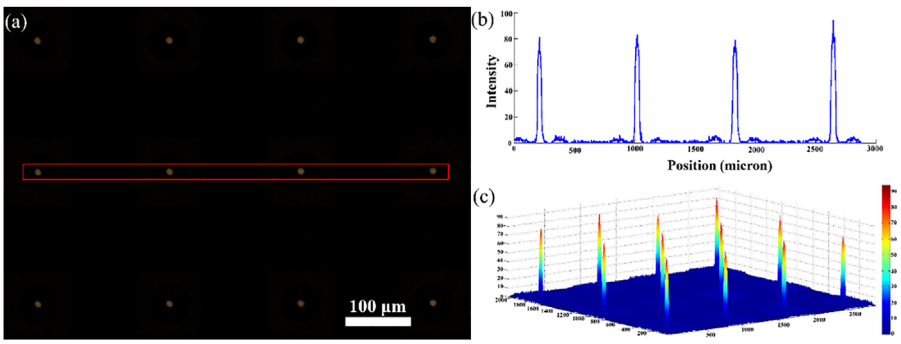

Figure 8. Test of the focal properties of the as-prepared MLA. a) Focal image of the MLA. b) The intensity distribution of the focal spots in select rectangular. c) 3D intensity distribution of the focal spots.

water function were integrated into a PDMS substrate. The microlenses were uniformly arranged on the PDMS surface, which were used for imaging. Meanwhile, the femtosecond laser-induced rough microstructures endowed the resultant MLAs with superhydrophobicity and self-cleaning ability. It was demonstrated that the anti-water MLAs could be easily washed clean with water droplet when the sample was polluted by contaminations. We believe that the fabricated anti-water and self-cleaning MLAs can be potentially used in endoscopic, solar cells, and many other optical systems that are often used in outdoor environment.

4. Experimental Section

Fabrication of Concave MLAs-Structured Template: A K9 glass substrate ($10 \times 10 \times 10\,mm^3$) was previously cleaned by acetone, alcohol, and deionized water in the ultrasonic water bath at ambient temperature for 5 min, respectively. The laser pulses with the center wavelength of 800 nm, duration of 50 fs and repetition rate of 1 kHz were generated from an amplified Ti: sapphire laser system (Coherent Libra-usp-he). The laser beam was focused onto the sample surface by an objective lens (50×, $NA = 0.60$, Nikon). The laser power was 5 mW and the point-by-point ablating manner was adopted. The exposure time of each ablation crater and the distance between the adjacent irradiating spots were set at constant value of 400 ms and 200 μm, respectively. After femtosecond laser treatment, the glass sheet was immersed in the hydrofluoric (HF) acid with a volume fraction of 10% for about 90 min.

Obtaining Convex MLAs on PDMS Substrate: By using the concave MLA-structured glass sheet as the template, a convex MLA was easily obtained on the PDMS surface via a template-replicated method. The liquid PDMS mixture was prepared by mixing the preploymer (DC-184A, Dow Corning Corporation) and curing agent (DC-184B, Dow Corning Corporation) with the volume ratio of 10:1. The PDMS mixture was poured onto the glass template and then cured at 80 °C for 90 min. Finally, the cured PDMS film was peeled from the glass template, resulting in a convex MLA on the PDMS surface.

Femtosecond Laser-Induced Surrounding Microstructure: The PDMS sample with the convex MLA was mounted on a three-dimensional (3D) transitional platform and the laser beam was focused on the sample surface by an objective lens (20×, $NA = 0.40$, Nikon). The laser power was kept at a fixed value of 20 mW. After laser ablation, the as-prepared PDMS MLA was orderly cleaned by acetone, alcohol, and deionized water in an ultrasonic bath for 10 min, respectively.

Morphology Analysis and Sample Characterization: The morphology of the sample fabricated by replica technique and femtosecond laser irradiation was characterized by a Quanta FEG 250 scanning electron microscope (SEM, FEI, America). The 3D and two-dimensional (2D) profiles of the sample were obtained by using a laser confocal scanning microscope (OLS4000, Olympus, Japan). The optical property of the fabricated PDMS MLAs was examined by an optical microscope system. The contact angle (CA) and sliding angle (SA) with 8 μL water droplet were measured by a JC2000D contact-angle system (Powereach, China) at ambient temperature using a sessile drop method. In order to decrease the measurement errors of the CAs and SAs, the average value was obtained by measuring five times on the same surfaces.

Supporting Information

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

Acknowledgements

This work was supported by the National Key Research and Development Program of China under the Grant no.2017YFB1104700, the National Science Foundation of China under the Grant nos. 51335008 and 61475124, U1630111, the Collaborative Innovation Center of Suzhou Nano Science and Technology and the International Joint Research Center for Micro/Nano Manufacturing and Measurement Technologies. The SEM work was done at International Center for Dielectric Research (ICDR), Xi'an Jiaotong University.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

anti-water, femtosecond laser, microlens array, self-cleaning, superhydrophobicity

Received: September 17, 2018
Revised: November 8, 2018
Published online: December 18, 2018

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