# Remote, selective, and in situ manipulation of liquid droplets on a femtosecond laser-structured superhydrophobic shape-memory polymer by near-infrared light 

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#### Abstract

Droplet manipulation plays a significant role in the fields of biomedical detection, microfluidics, and chemical engineering. However, it still remains a great challenge to simultaneously achieve remote, selective, and in situ droplet manipulation on the same surface. Here, $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles were doped in a shape-memory polymer (SMP) to prepare a photothermal-responsive $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite which showed remarkable near-infrared (NIR) light-triggered shape-memory property. Superhydrophobic micropillar array was constructed on such $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composite through femtosecond laser microfabrication and fluoroalkylsilane modification. The surface wettability of the as-prepared surface can transform from a low-adhesive sliding state to a high-adhesive pinning state as the micropillars are deformed by pressing. Interestingly, the deformed micropillars can stand up and restore to their original morphology under remote NIR light irradiation, resulting in the reversible and repeatable recovery of the ultralow-adhesive superhydrophobicity. With such light-triggered wettability switching, the droplets pinning on the sample surface can be remotely, selectively, and in situ released. Furthermore, the superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface is successfully applied in lossless liquid transfer, selective droplet release, and droplet-based microreactor. The as-fabricated superhydrophobic surfaces with NIR light-controlled reversible wettability will hold great promise in the fields of liquid manipulation, lab-on-a-chip, and microfluidics. droplet manipulation, superhydrophobicity, shape-memory polymer, femtosecond laser, light responsive


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## 1 Introduction

Droplet manipulation has aroused increasing attention because of its broad applications in droplet transfer [1-3], biological monitoring [4-6], lab-on-a-chip [7,8], and microfluidic devices [9-11]. Superwetting surfaces have been widely used in droplet manipulation [12-16]. Like the lotus leaf and rose petal in nature, superhydrophobic surfaces can exhibit different dynamic wettabilities, such as ultralow water adhesion and ultrahigh water adhesion [2,17]. Water

[^0]droplets roll off easily on the lotus leaf. Such low-adhesive superhydrophobic surfaces usually have excellent selfcleaning ability. By contrast, rose-petal-like superhydrophobic surfaces show high water adhesion, which can be functionalized as a "mechanical hand" to grasp and transport small water droplets. For example, Cheng et al. [18] fabricated a sticky superhydrophobic polydimethylsiloxane (PDMS) film by the combination of electrodeposition and casting replication technique. The water droplet could strongly attach to the sample surface; thereby the droplet was transported from a low-adhesive superhydrophobic surface to a higher-adhesive superhydrophobic
surface by using this sticky superhydrophobic surface, without any mass loss. Liu et al. [19] also achieved the nonloss transfer of water droplet by the superhydrophobic copper surface with high water adhesion. Lee et al. [20] fabricated a high-adhesive superhydrophobic nanowire array to achieve droplet transfer and mixture. By using the highadhesive superhydrophobic surfaces, water droplets can be transported from a lower-adhesive surface to a higheradhesive surface, but such transfer process is irreversible. The reported sticky superhydrophobic surfaces can only release a droplet to a substrate with a higher adhesion and cannot achieve in situ droplet release. For practical applications, it is greatly desirable to realize in situ reversible droplet manipulation on a single sample surface. Sun et al. [21] developed a novel superhydrophobic PDMS micropillar array whose wettability could be reversibly switched between sliding state and pinning state by tuning the surface curvature. The water adhesion of the surface gradually decreased with increasing the surface curvature, and thereby the water droplets could be in situ released as the curvature exceeded a critical value. Shape-memory polymer (SMP) is an important class of smart materials that can reversibly change its shape between permanent state and temporary state upon external environment [22,23]. Such shape-recoverable substrate provides a potential candidate to reversibly tune the surface wettability (e.g., switchable water adhesion) by regulating the morphology of SMP microstructures [24-27]. For example, Liu et al. [24] prepared a superhydrophobic surface by constructing micropillar structures on the SMP substrate. The wettability of the surface can be reversibly switched between the sliding state and the pinning state through alternate pressing and heating the micropillars. Recently, Wu et al. [28] integrated a superhydrophobic SMP microcone array with a silver nanowire heater circuit. The wettability of the surface could be in situ transformed between sliding state and pinning state under circuit heating, thus realizing the in situ release of water droplets. Although the abovementioned smart surfaces can achieve droplet release in situ, the triggering process must be operated at a very near distance and it is difficult to selectively manipulate specific droplets on a sample surface. As a typical noncontact manner, remote manipulation enables high spatial and temporal controllability [23,29-31]. Simultaneously achieving remote, selective, and in situ manipulation of liquid droplets on a superhydrophobic surface is of great significance to broaden the application fields of droplet manipulation technology in practice, and to date, such methods and surfaces have been rarely reported.

In this study, $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles were doped into a ther-mal-responsive SMP matrix to endow the SMP composite with photothermal responsive property. Micropillar array was prepared on the surface of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composite by femtosecond laser processing, which showed low-adhesive
superhydrophobicity after fluoroalkylsilane modification. The micropillars could be inclined upon pressing treatment and recover to original state just by near-infrared (NIR) light irradiation. As a result, the surface wettability was reversibly transformed between low-adhesive superhydrophobic state and high-adhesive pinning state. Water droplets pinning on the sample surface could be remotely, selectively, and in situ released by NIR light irradiation. Based on the unique lighttriggered wettability transformation, lossless liquid transfer, selective liquid release, and droplet-based microreactor were achieved by using the superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface.

## 2 Experimental

### 2.1 Preparation of the $\mathrm{Fe}_{3} \mathrm{O}_{\mathbf{4}}$-SMP composite

The blank SMP resin matrix was prepared by thoroughly mixing the diglycidyl ether of bisphenol A (Nantong Xingchen Synthetic Material Co., Ltd., China), n-octylamine (J\&K Scientific Ltd), and $m$-xylylenediamine (J\&K Scientific Ltd., China) at a molar ratio of 5:1:2. Then, the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles (with a diameter of $200-300 \mathrm{~nm}$, Aladdin Industrial Corporation, USA) were dispersed into the SMP resin matrix with mechanically stirring for about 10 min , as shown in Figure 1(a). After degassing treatment, the dispersion was poured into a Teflon mold and successively cured at $60^{\circ} \mathrm{C}$ for 2 h and then at $100^{\circ} \mathrm{C}$ for 1 h to obtain the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite, as shown in Figure 1(b, c).

### 2.2 Formation of micropillar array

Femtosecond laser processing was utilized to generate micropillars on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface. The laser pluses (a pulse width of 50 fs , a central wavelength of 800 nm , and a repetition rate of 1 kHz ) were produced from a Ti:sapphire laser system (Libra-USP-HE, Coherent, USA) and were focused onto sample surface via an objective lens $(\times 5$, $\mathrm{NA}=0.15$, Nikon, Japan). The whole surface of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ SMP substrate was firstly processed by a femtosecond laser at the laser power of 10 mW , the scanning speed of $6,000 \mu \mathrm{~m} / \mathrm{s}$, and the interval of scanning lines of $6 \mu \mathrm{~m}$. Then, the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface was selectively ablated by femtosecond laser to create micropillar array. As shown in Figure 1 (d), the orthogonally-crossed femtosecond laser line-by-line ablation manner was exploited. The interval of scanning lines was adjusted from 2 to $10 \mu \mathrm{~m}$, the laser power was adjusted from 30 to 70 mW , and the scanning speed was constant at $4,000 \mu \mathrm{~m} / \mathrm{s}$. During the femtosecond laser processing, the laser selectively ablated the sample surface. The ablated region was lower than the untreated region because of the laser-induced material removal, so the rest untreated region finally developed to a micropillar array on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ SMP composite. After ultrasonically cleaning, the laser-
structured samples were fluorinated by placing in a closed container together with several drops of $1 H, 1 H, 2 H, 2 H$-perfluorodecyltrichlorosilane (Aladdin Industrial Corporation) for 4 h at room temperature.

### 2.3 Manipulation of the micropillar array

The NIR light (wavelength=808 nm, FU808AD2000-F34, Shenzhen Fuzhe Technology Co., Ltd., China) was used to irradiate the sample, which makes the micropillar-structured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite become soft. Then, the soft sample was pressed by a flat surface to cause the micropillars lean to one side. Under the pressure, the composite was cooled down to fix the deformed shape of the micropillars. The recovery of the micropillar morphology was simply realized by a NIR light re-irradiation process.

### 2.4 Characterization

A thermal infrared camera (VarioCAM ${ }^{\circledR}$ ) was used to measure the surface temperature of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite under NIR light irradiation. Dynamic mechanical analysis (DMA) (DMA242E, Netzsch) was exploited to characterize the storage modulus and $\tan \delta$ of the sample. The surface morphology was observed by a scanning electron microscope (SEM) (FlexSEM-1000, Hitachi, Japan). The values of contact angle (CA) and sliding angle (SA) were obtained by a contact angle measurement (JC2000D, PoweReach) with the water volume of $6 \mu \mathrm{~L}$.

## 3 Results and discussion

### 3.1 Preparation and property of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite

Introducing light-absorbing additives into the thermalresponsive SMP is a common method of preparing photoresponsive SMP [32-34]. The epoxy-based SMP used here is a typical thermal-responsive polymer, whose shape can recover from deformed state to original state above its glass transition temperature ( $T_{\mathrm{g}}$ ). Light can travel a very long distance and can be easily converted into heat energy. $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles can absorb photon energy and convert it into thermal energy, thereby increasing the sample temperature [35]. To endow the thermal-responsive SMP matrix with photothermal responsive property, $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles were introduced into such SMP substrate, as shown in Figure 1(ac). A certain amount of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles were added into the mixture of the SMP prepolymer and curing agent, and thoroughly stirred to form a homogeneous dispersion (Figure 1(a)). Then the dispersion was carefully poured into a shallow groove on a Teflon mold, which was pre-placed in a vacuum oven in order to completely remove air bubbles in
the dispersion (Figure $1(\mathrm{~b})$ ). The dispersion was cured by heating treatment at $60^{\circ} \mathrm{C}$ for 2 h and then at $100^{\circ} \mathrm{C}$ for 1 h . Finally, the solid $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite was obtained by peeling off from the mold (Figure 1(c)).

As a typical photothermal conversion material, black $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles have strong light-absorption ability in the NIR spectrum [36-39]. Under NIR light irradiation, $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles can absorb light energy and immediately convert into thermal energy, which is well known as the photothermal effect [40-42]. As shown in Figure 2(a), the thermal image indicates that NIR light irradiation can increase the surface temperature of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composite. With extending the irradiation time, the surface temperature of the sample gradually increases. The content of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles has a great influence on the photothermal behavior of the composite. After NIR light irradiation (light intensity: $1.7 \mathrm{~W} / \mathrm{cm}^{2}$, irradiation distance: 45 cm ) for 10 s , the surface temperatures of different samples with $0.2 \mathrm{wt} \%, 1$ $\mathrm{wt} \%$, $2 \mathrm{wt} \%$, and $4 \mathrm{wt} \% \mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles reached up to $78,108,137$, and $140^{\circ} \mathrm{C}$, respectively (Figure 2(b)). The results indicate that a SMP composite with higher $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticle content tends to have a higher surface temperature under the same light irradiation time. The photothermal ability of the $2 \mathrm{wt} \% \mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite is close to that of the $4 \mathrm{wt} \% \mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composite, so the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ SMP composite with $2 \mathrm{wt} \% \mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles was used in subsequent experiment.

DMA is usually utilized to measure the thermal and mechanical properties of a polymer. From the $\tan \delta$ curve in Figure 2(c), it can be found that the $T_{\mathrm{g}}$ of the blank SMP is about $56^{\circ} \mathrm{C}$. The addition of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles makes the $T_{\mathrm{g}}$ of the resultant $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite decrease to $53^{\circ} \mathrm{C}$. Such slight $T_{\mathrm{g}}$ decline is attributed to the fact that the doped nanoparticles hinder the crosslinking of the SMP molecular chains to some extent during the polymerization process [35]. As the temperature increases from 20 to $80^{\circ} \mathrm{C}$, the phase state of the polymer will dramatically change from glassy state to rubbery state, and thus the storage modulus of the blank SMP declines from 3.3 GPa to 3.1 MPa while that of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite declines from 3.9 GPa to 1.3 MPa (Figure 2(c)). The blank SMP and the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite have approximate equivalent $T_{\mathrm{g}}$ and storage modulus, so the doping of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles has little effect on the thermal and mechanical properties of the SMP substrate.

To demonstrate the photo-responsive ability of the $\mathrm{Fe}_{3} \mathrm{O}_{4}{ }^{-}$ SMP composite, a composite with the dimension of 33 mm $\times 4.3 \mathrm{~mm} \times 1.3 \mathrm{~mm}$ (length $\times$ width $\times$ thickness) was heated and stretched up to $27 \%$ strain and then immediately cooled down to lock the deformed shape (Figure 2(e, f)). A blank SMP with the same dimension was used as a comparison group. Upon NIR light irradiation (light intensity: 2.6 W/cm ${ }^{2}$, irradiation distance: 30 cm ), the stretched $\mathrm{Fe}_{3} \mathrm{O}_{4}$ -


Figure 1 Illustration of the preparation process of the superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillars with NIR light-triggered reversible wettability. (a-c) Preparation process of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. (d) Preparation of micropillars on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite by femtosecond laser. (e, f) Reversible switching of wettability between sliding state and sticky state through pressing and NIR-light irradiation processes (color online).


Figure 2 Photothermal effect and shape-memory ability of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. (a) Thermal images of irradiating a Fe $\mathrm{O}_{4}$-SMP composite by NIR light for different time. (b) Influence of the content of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles on the photothermal behavior of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composites. (c) DMA curves for the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite and the blank SMP. (d) Reversible deformation and recovery of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP strip between original shape and various deformed shapes. (e-g) Deformation and recovery of the $\mathrm{Fe}_{3} \mathrm{O}_{4}-\mathrm{SMP}$ composite under stretching and light irradiation treatments. The blank SMP is used as a control sample (color online).

SMP composite could recover to its original length immediately (Figure 2(g)). In contrast, the blank SMP main-
tained the stretched state even after continuous NIR light exposure for some minutes (Figure $2(\mathrm{~g})$ ). Therefore, the
doping of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles enables the SMP composite to have excellent photo-responsive ability. In addition to the simple stretching deformation, the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composite could also be temporarily programmed into other different complex shapes, such as the twisted shape, " $\infty$ " shape, circle shape, and "M" shape (Figure 2(d)). The composite with various temporary shapes could completely restore to its original shape via NIR light irradiation because of the excellent photo-responsive shape-memory property of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite (Figure 2(d)).

### 3.2 Superhydrophobic microstructure and wettability switching

Femtosecond laser direct writing is utilized to prepare the micropillar structures on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite via an orthogonally-crossed line-by-line ablation method [15,16,31] (Figure 1(d)). During the scanning process, the adjacent laser-pulse-induced craters were strongly overlapped, thus resulting in the dramatic material removal. As a result, the ablated region is lower than the untreated region. The preprogramed rectangular scanning path can be precisely controlled by a computer program. Through selective femtosecond laser scanning, the laser-ablated region develops to the rectangular microgroove-patterned structure on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. The rest untreated region naturally becomes the ridge structures between adjacent microgrooves. After that, the sample is rotated by $90^{\circ}$ in the $X-Y$ plane and the abovementioned selective femtosecond laser scanning process is repeatedly executed. The remaining unablated region finally forms the micropillar array structure on the sample surface.

Figure 3(a, b) display the SEM images of the femtosecond laser-structured micropillar array. The micropillar array was prepared at the laser power of 40 mW , the scanning speed of $4 \mathrm{~mm} / \mathrm{s}$, and the interval of scanning lines of $2 \mu \mathrm{~m}$. The asprepared micropillars have a top diameter of $20 \mu \mathrm{~m}$ and an adjacent space of $40 \mu \mathrm{~m}$ (Figure 3(a)). The inset image in Figure 3(b) shows that the height of the micropillars is about $57 \mu \mathrm{~m}$. The whole surface of the micropillars is covered by abundant hierarchical micro/nano-structures, which originates from the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles in the SMP composite and the particle ejection during the laser ablation process (Figure 3(b)). If a water droplet was dropped onto the resultant surface, the droplet would spread out quickly with a final CA about $0^{\circ}$. Fluoroalkylsilane modification was utilized to lower the surface free energy of the micropillar array (Figure 1(e)). After fluoroalkylsilane treatment, the CA on the structured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite increased to $153.7^{\circ}$ $\pm 1.2^{\circ}$ (Figure 3(c)). Water droplets could readily roll off when the surface was inclined by about $7^{\circ}$, revealing lowadhesive superhydrophobicity (Figure 3(c)).
The wettability of the superhydrophobic micropillars can
be reversibly converted through regulating the micropillar morphology (Figure 1(f)). Upon heating above $T_{\mathrm{g}}$, the composite became soft and the micropillar array on the substrate could be easily deformed under the action of an external force. The micropillars were leaned to one side after pressing treatment, as shown in Figure 3(d, e). At this time, the CA on the resultant surface decreased to $140.9^{\circ} \pm 1^{\circ}$ because the increased contact area between the water droplet and the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite (Figure 3(f)). Water droplets could firmly adhere to the sample surface even if the surface was upright or overturned, showing high-adhesive pinning state (Figure 3(f)). Interestingly, the surface morphology of the micropillars could completely restore to stand-up state through NIR light irradiation for about 3-5 s (light intensity: 2.6 W/cm ${ }^{2}$, irradiation distance: 30 cm ) (Figure 3(a, b)). As a result, the surface re-obtained its original low-adhesive superhydrophobicity (Figure 3(c)). This recovering process is driven by the excellent light-responsive shape-memory ability of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. The wettability can also be switched from the high-adhesive pinning state to the lowadhesive sliding state by NIR light even at a long irradiation distance of 2 m , showing strong remote liquid manipulation ability. Moreover, this reversible wettability conversion can be repeated at least 20 times (Figure $3(\mathrm{~g}, \mathrm{~h})$ ). These results indicate that the micropillar-structured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite has extraordinary reversible and controllable wettability.

The switching mechanism of the wettability on the structured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite is illustrated in Figure 4. It is well known that $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticle is a kind of photothermal material, which can absorb photon energy and immediately convert it into thermal energy under NIR light irradiation [40-42]. This rapid conversion from photon energy to thermal energy is ascribed to the electron-phonon and phononphonon processes of $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles during NIR light irradiation [43]. At room temperature, the molecular chain conformation in the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite is at the thermodynamically stable state [22] (Figure 4(a)). The upright micropillars on the femtosecond laser-structured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite are at the permanent shape. The surface of the micropillars is covered with abundant hierarchical micro/ nano-structures (Figure 3(b)). Water droplets can only touch the top portion of the micropillars due to the trapped air cushion between the water droplets and the micropillarstructured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. At this time, the contact model between the water droplet and $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array is a typical Cassie contact state [44] (Figure 4(e)). As a result, the water droplet can slide easily on the sample surface, displaying the low-adhesive superhydrophobicity. When the composite is exposed to NIR light, $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles firstly absorb light and then the surrounding polymer molecules quickly get heated (Figure 4(b)). As the temperature of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite increases above


Figure 3 Reversibly switching the surface morphology and the wettability of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillars via alternate pressing treatment and NIR-light irradiation. (a, b) $45^{\circ}$-tilted SEM images of the original/recovered micropillars on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. The inset in (b) is the cross-sectional SEM image of the micropillars. (c) Wettability of a water droplet on the original/recovered sample surface. (d, e) $45^{\circ}$-tilted SEM images of the deformed micropillars. (f) Wettability of a water droplet on the deformed sample surface. Reversible switching of (g) CA and (h) SA with the repeated pressing and NIR-light irradiation processes (color online).
$T_{\mathrm{g}}$, the molecular chains in the SMP are greatly activated and the composite becomes soft (Figure 4(b)). In this case, the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite can be easily deformed under external pressure (Figure 4(c)). For example, the micropillars can be leaned to one side (Figure 4(f)). Once turning off the NIR light, the composite temperature gradually declines below $T_{\mathrm{g}}$ and the action of SMP molecular chains is largely restricted [22]. The micropillar array is temporarily locked in the deformed morphology (Figure 4(d, f)). When water droplets are dropped on the surface, the water droplet will contact with the most region of the inclined micropillars, not just the top surface of the micropillars. The dramatically
increased contact region between the water droplet and the SMP micropillars results in the high-adhesive wettability state. Water droplets would highly adhere to the deformed micropillars even if the sample was vertical or completely overturned, showing high-adhesive pinning state. As a result, the proportion of the air layer embedded between the water droplet and the micropillar array is significantly reduced. The wettability of the surface transformed from the original low-adhesive Cassie state to the high-adhesive CassieWenzel state [45] (Figure 4(f)). Upon returning on the NIR light, $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles will reheat the surrounding polymer molecules, thus facilitating the recovery of surface


Figure 4 Mechanism of the shape-memory ability and wettability conversion of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite under NIR light irradiation. Mechanism of the NIR light-triggered shape-memory process of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP composite: (a) original $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP molecular crosslinking network, (b) the $\mathrm{Fe} \mathrm{O}_{3} \mathrm{O}_{4}$ - SMP molecular crosslinking network activated by NIR light, (c) the activated $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP molecular crosslinking network pressed by an external force, and (d) the deformed $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP molecular crosslinking network fixed by cooling. The curved lines represent the molecular crosslinking network of the polymer. The black dots are $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles. Wetting state of a water droplet on (e) the original/recovered $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillars and (f) the deformed $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillars (color online).
morphology and wettability.

### 3.3 Influence of laser parameters on micropillar morphology and wettability

Femtosecond laser processing is a flexible and effective tool which can design various 3D hierarchical micro/nanostructures on the substrate surface. The height of the asprepared micropillars can be adjusted by changing the laser power and the interval of scanning lines during laser processing. When the laser power rises from $30,40,50,60$, and to 70 mW , the micropillar height increases from $28,35,43$, 52, and to $60 \mu \mathrm{~m}$ under the constant scanning line interval of $4 \mu \mathrm{~m}$ (Figure 5(a)). Furthermore, the micropillar height almost linearly increases with the laser power, which agrees with the fact that the higher laser power leads to the stronger material removal [46]. With the laser power increasing from 30 to 70 mW , the CA values on the sample surfaces are all above $150^{\circ}$ and the SA values are all below $10^{\circ}$ (Figure 5(c)). The surfaces with different micropillar heights maintain superhydrophobicity and ultralow water adhesion. The micropillar height gradually decreases with the rise of the interval of scanning lines. When the interval of the scanning lines increases from $2,4,6,8$, and to $10 \mu \mathrm{~m}$, the micropillar height decreases from $57,35,30,20$, and to $17 \mu \mathrm{~m}$ under the constant laser power of 40 mW (Figure 5(b)). The decline of micropillar height is owing to the reduction in the number of laser pulses per unit area with the increasing of scanning line
interval $[47,48]$. It can be seen that all the sample surfaces display low-adhesive superhydrophobicity ( $\mathrm{CA}>150^{\circ}$, $\mathrm{SA}<10^{\circ}$ ) as the scanning line interval ranges from 2 to $10 \mu \mathrm{~m}$ (Figure 5(d)). The abovementioned results indicate that the micropillar height can be facilely adjusted by changing the laser power and the interval of scanning lines, and the micropillar height has little effect on the surface wettability.

The space between the micropillars is determined by the size of the laser-ablated region while the diameter of the micropillars depends on the size of the untreated region. These two parameters can be freely designed during the laser processing. The influence of the micropillar space on the surface wettability was studied under a constant micropillar diameter of $20 \mu \mathrm{~m}$ and a micropillar height of $35 \mu \mathrm{~m}$. With the micropillar space increasing from $40,60,100,140,180$, and to $220 \mu \mathrm{~m}$, the CA values decrease from $153.3^{\circ} \pm 1.3^{\circ}$, $151.3^{\circ} \pm 1.7^{\circ}, 152^{\circ} \pm 1.8^{\circ}, 153.8^{\circ} \pm 0.9^{\circ}, 150.5^{\circ} \pm 1.8^{\circ}$, and to $147.3^{\circ} \pm 0.6^{\circ}$, while the SA values are all below $10^{\circ}$ (Figure 5 (e)). As the micropillar space increases, the water droplet will be gradually embedded into the intervals of the micropillars. As a result, the contact region between the water droplet and the sample surface increases, which results in a slight decline of CA value. It is indicated that superhydrophobicity can be obtained with the micropillar space ranging from 40 to $180 \mu \mathrm{~m}$ (Figure 5(e)).

Compared to the micropillar space, micropillar diameter has a great effect on the dynamic wettability of the asprepared surface. As shown in Figure 5(f), when the micropillar diameter increases from $20,50,90,130$, and to


Figure 5 Influence of processing parameters on the surface morphology and wettability. (a) Relationship between the micropillar height and the laser power. (b) Relationship between the micropillar height and the interval of scanning lines. The dependence of surface wettability on (c) the laser processing power, (d) the interval of scanning lines, (e) the micropillar space, and (f) the micropillar diameter (color online).
$170 \mu \mathrm{~m}$ (micropillar spacing $=40 \mu \mathrm{~m}$ and micropillar height= $35 \mu \mathrm{~m}$ ), all the CA values maintain above $150^{\circ}$. However, the SA values obviously increase from $6.4^{\circ} \pm 0.3^{\circ}, 23.1^{\circ} \pm 3.2^{\circ}$, $30.3^{\circ} \pm 0.9^{\circ}, 30.5^{\circ} \pm 6.4^{\circ}$, and to $34.2^{\circ} \pm 1.4^{\circ}$, indicating that the water adhesion of the surface is gradually increased (Figure 5 (f)). The dramatic increase of water adhesion on the sample surfaces is due to the increase of contact region between the water droplets and the micropillars.

### 3.4 Light-triggered droplets manipulation

The light-triggered wettability-conversion property enables the as-prepared superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surfaces to have the advanced ability of remote droplet manipulation in comparison to the traditional thermal-responsive super-
hydrophobic SMP surfaces [24,27]. As displayed in Figure 6 (a), a water droplet on the original superhydrophobic micropillar array can easily slide off with a small tilted angle or a slight vibration (Figure 6(b), Movie S1, Supporting Information online). As some micropillars on the sample surface are deformed, such deformed part becomes a highadhesive region. The water droplet can firmly pin on this region even though the sample is completely overturned (Figure 6(c)). Surprisingly, the captured droplet can be released through NIR light irradiation (Figure 6(d, e)). To demonstrate the in situ droplet capture and release process, a $10 \mu \mathrm{~L}$ water droplet was pre-placed on a low-adhesive superhydrophobic substrate (e.g., original superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface). The superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface with deformed micropillars was slowly moved down


Figure 6 In situ droplet release on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array triggered by NIR light. (a) Illustration of a water droplet rolling on the upright micropillar array. (b) Sliding process of a droplet on the original superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillars with an inclination angle of $10^{\circ}$. Milk is used here for clear observation. Illustration of the in situ release of a droplet through NIR-light irradiation: (c) the droplet pinning on the deformed $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillars, (d) irradiating the region underneath the pinned droplet by NIR light, and (e) the pinned droplet detaching from the sample surface and falling off freely. (f) Time-sequence images of a water droplet ( $10 \mu \mathrm{~L}$ ) detaching from the deformed micropillar array and falling freely triggered by NIR light irradiation (color online).
until it touched the water droplet. Then, the sample was lifted up. Owing to the high water adhesion of the deformed region, the water droplet detached from the original substrate and pinned on the deformed superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface, like being successfully captured by the sample surface. Moreover, the captured droplet could be in situ released easily. Once the region underneath the pinned water droplet was irradiated by NIR light (Figure 6(d)), the deformed micropillar array would instantly recover to the original upright state (Figure 6(e)). The contact region between the water droplet and the micropillar array was dramatically decreased. With the recovery of the original low-adhesive superhydrophobicity of the micropillar array, the captured droplet fell off freely from the sample surface (Figure 6(e, f) and Movie S2). In this process, the captured droplets are released through remote light irradiation instead of direct manipulation. This release process can even be triggered by light from a long distance of 2 m . The properties of in situ droplet capture and release enable the femtosecond laserstructured $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array to have great promise in remote liquid manipulation.

Since the light-irradiated position can be flexibly controlled, thereby causing the selective manipulation of droplet on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array. As an example, the process of selectively releasing two droplets on one asprepared superhydrophobic surface is shown in Figure 7 and Movie S3. Two different regions of the micropillars on the
superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface were deformed and exhibited high water adhesion by pressing treatment. Two water droplets ( A and B ) were respectively dispensed onto these two regions and thus tightly adhered to the sample surface in advance (Figure 7(a)). Even if the sample was greatly tilted (e.g., at $65^{\circ}$ ), the droplets still firmly stuck on the sample surface (Figure 7(e)). The release of either droplet A or B could be realized by selectively irradiating the corresponding region underneath the droplets. For instance, as long as the region underneath the droplet B was irradiated by NIR light (Figure 7(a, f)), the deformed micropillars in this region would immediately recover (Figure 7(b)). With the recovery of ultralow-adhesive superhydrophobicity, the movement of droplet B was triggered and the droplet rolled away the sample surface, achieving rapid release of this droplet (Figure 7(b, g)). The droplet A also could be released like the droplet B. Once the NIR light was switched to irradiate the region underneath the droplet A (Figure 7(c, h)), the movement of the droplet A was also triggered, so this droplet rolled off on the sample surface quickly (Figure 7(d, $\mathrm{i}, \mathrm{j})$ ). The droplet A could be released first before droplet B through irradiating the region beneath the droplet A first. In addition to releasing two droplets, the surface can also be used to selectively release more droplets. The surface with selective droplets-release property will have important practical values in droplet manipulation technology.

Taking advantage of the remote and selective ability to


Figure 7 Selective droplet release on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array controlled by NIR light. (a-d) Illustration of the selective release of droplets via NIR light irradiation. (e-j) Time-sequence images of selective releasing a water droplet ( $10 \mu \mathrm{~L}$ ) from the surface tilted at $65^{\circ}$. Milk is used here for clear observation (color online).
manipulate small droplets, the as-fabricated superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array can also be utilized as a platform for achieving droplet coalescence or mergence. As shown in Figure 8(a), two different regions of the micropillars on the superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP surface were deformed and exhibited high water adhesion by pressing treatment. Two different droplets (A and B ) were respectively dropped on two deformed regions on the same sample surface. The droplet A was at the top region of the surface, while the droplet B was at the bottom region. When the NIR light irradiated the region of droplet A , this droplet would slide off on the surface (Figure 8(b)). As the droplet A arrived at the bottom region, the droplet A and B would contact and merge into a larger droplet (Figure 8(c)). Based on this droplet coalescence process, a microreactor was designed on the superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array, as shown in Figure $8(\mathrm{~d}-\mathrm{i})$ and Movie S4. A sodium citrate droplet was dropped on the top region of the surface, and a phenol red droplet was dropped on the bottom region (Figure $8(\mathrm{~d})$ ). The sample was tilted at about $20^{\circ}$. Once the region underneath the sodium citrate droplet was irradiated by NIR light (Figure 8(e)), this droplet started to roll down
(Figure $8(\mathrm{f}-\mathrm{h})$ ) and thus met with the phenol red droplet (Figure 8(i)). Finally, the sodium citrate droplet and the phenol red droplet merged into a large droplet. Meanwhile, the color of the merged droplet immediately turned from yellow to red due to the chromogenic reaction between sodium citrate and phenol red (Figure 8(i)). Compared with traditional chemical reaction, the droplet-based microreactor has many advantages including reduced use of chemical reagents, high sensitivity, and low operation cost [49-51]. Such microreactor can also be applied for other chemical reactions, which shows promising prospects in biological detection and chemical synthesis.

## 4 Conclusions

In summary, a novel superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array with NIR light-triggered reversible water adhesion is prepared by doping $\mathrm{Fe}_{3} \mathrm{O}_{4}$ nanoparticles into a thermal-responsive SMP material and femtosecond laser processing. The original superhydrophobic $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillar array shows low-adhesive superhydrophobicity


Figure 8 Droplet coalescence on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillar array. Illustration of the coalescence of two droplets on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$ - SMP micropillars: (a) droplet A and B pinning on the deformed $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillars, (b) the pinned droplet A starting to roll on the surface by NIR-light irradiating the region underneath the droplet A , and (c) droplet A and B contacting and merging into a larger droplet. Droplet-based microreactor between sodium citrate solution $(10 \mu \mathrm{~L})$ and phenol red solution $(6 \mu \mathrm{~L})$ on the surface of $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillars: (d) the droplets of sodium citrate and phenol red pinning on the deformed $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP micropillars, (e) irradiating the region underneath the sodium citrate droplet by NIR light, ( $\mathrm{f}-\mathrm{h}$ ) the process of sodium citrate droplet sliding off on the sample surface, and (i) the reaction between sodium citrate droplet and phenol red droplet after contacting with each other. The surface is tilted at $20^{\circ}$ (color online).
with a CA of $153.7^{\circ} \pm 1.2^{\circ}$ and a SA of $7.5^{\circ} \pm 0.7^{\circ}$. The micropillar array on the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite can be easily deformed (i.e., leaned to one side) by pressing treatment. The sample surface thus switches to high-adhesive state with the water droplets firmly pinning on the sample surface (SA $=90^{\circ} / 180^{\circ}$ ). The NIR light is able to remotely and locally heat the deformed micropillars, and thereby the surface morphology and the wettability are selectively recovered because of the light-responsive shape-memory ability of the $\mathrm{Fe}_{3} \mathrm{O}_{4}$-SMP composite. This reversible wettability conversion between low-adhesive superhydrophobic state and highadhesive pinning state can be repeated at least 20 times. Furthermore, the surface enables the wettability to switch from the high-adhesive pinning state to the low-adhesive sliding state by NIR light even at an irradiation distance of 2 m . Compared with previously reported wettability-tunable surfaces, the NIR light-responsive superhydrophobic surface can realize wettability conversion in a remote, selective, and in situ manner. Water droplets pinning on the sample surface can be remotely, selectively, and in situ released by NIR light irradiation. Taking advantage of the unique NIR light-triggered wettability transformation, the as-fabricated surface can be utilized for lossless liquid transfer, selective liquid
release, and droplet-based microreactor. It is anticipated that such surfaces will have promising prospects in liquid manipulation, lab-on-a-chip, and microfluidics.

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