Femtosecond Laser Weaving Superhydrophobic Patterned PDMS Surfaces with Tunable Adhesion

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ABSTRACT: We present a rapid, facile, and simple method to realize superhydrophobic patterned polydimethylsiloxane (PDMS) surfaces with tunable adhesion by a femtosecond laser. These surfaces are composed of superhydrophobic laser-induced structures and hydrophobic unstructured square array. The femtosecond laser structured domain shows superhydrophobicity with ultralow water adhesion, while the nonstructured flat PDMS shows ordinary hydrophobicity with ultrahigh water adhesion. By adjusting the relative area fraction of laser structured and nonstructured domains, the as-prepared superhydrophobic surfaces show tunable water adhesion that ranges from ultralow to ultrahigh, on which the sliding angle can be controlled from 1° to 90° (a water droplet cannot slide down even when the as-prepared surface is vertical or turned upside down). The tunable adhesive superhydrophobic surfaces achieved by femtosecond laser microfabrication may be potentially used in microfluidic systems to modulate the mobility of liquid droplets.

1. INTRODUCTION

Superhydrophobic surfaces with a water contact angle (CA) higher than 150° have received considerable attention due to their importance in both fundamental research and practical application.¹⁻⁸ Among these superhydrophobic surfaces, two kinds of extremely superhydrophobic cases exist: ultralow water adhesion and ultrahigh water adhesion.⁹⁻¹² The lotus leaf, with an ultrahigh CA but ultralow water adhesion, is demonstrated as the ideal water-repellent superhydrophobic surface.^{13,14} Water droplets on such surfaces can easily roll off to remove loosely adherent dirt particles and debris from the surfaces if the substrate is slightly tilted. This phenomenon is well-known as the self-cleaning effect.¹³ Contrary to this characteristic, a new kind of sticky superhydrophobic surface with ultrahigh water adhesion like a rose petal has recently been reported.¹⁵ On this surface, the CA of the water droplet is usually above 150°, while the water droplet would be stuck and would not roll off even with the surface upside down. The high-adhesion superhydrophobic surfaces can provide some fascinating applications in manipulating liquids at the micrometer scale. Recently, intense interest has been focused on the smart superhydrophobic surfaces exhibiting tunable adhesive forces

and sliding angles (SAs) because the tunable adhesion allows the manipulation of water droplets on superhydrophobic surfaces.^{16,17} The surfaces are expected to have particular applications in many fields, including no loss microdroplet transportation,^{18–20} cell adhesion,²¹ biochemical separation,²² and microfluidic channels with diminished resistance.^{23,24}

In general, the water adhesive property of a superhydrophobic surface is mainly governed by two factors: the surface geometrical structure and chemical composition and, by dynamically tuning the two factors, the water adhesion could be effectively tuned.^{25–28} For instance, Jiang et al. prepared a superhydrophobic aligned polystyrene nanotube layer and obtained a controllable transition between high adhesive pinning and low adhesive rolling states.^{18,29} Sun et al. realized slippery-to-sticky superhydrophobic surfaces by controlling the reaction time or the chain length of the thiol based on the reaction between an alkyl thiol and hierarchical structured Cu(OH)₂ substrates.³⁰ Liu et al. reported a superhydrophobic

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Figure 1. (a) Schematic of experimental setup. (b) Schematic illustration of the fabrication of hierarchical rough structure.

MnO₂ nanostructured film with controllable adhesion by fabricating different patterns of MnO₂ nanocrystallites. Chen et al. reported an electrophoretic deposition method to form homogeneous and stable TiO₂-based nanobelt thin films. By adjusting the deposition time, the superhydrophobic coatings could be made "sticky" and "nonsticky" for the water droplet on the surface.³² Xu et al. prepared a superhydrophobic cauliflower-like morphology by introduction of organic groups in silica nanospheres, and the adhesion could be modulated by adjusting the phenyl group content.³³ Wang et al. realized tunable adhesion in superhydrophobic nanostructured Co₃O₄ films by simply rubbing the as-prepared films.³⁴ However, most reported methods used to fabricate superhydrophobic surfaces with tunable adhesion generally require complex fabrication processes and have tight restrictions on materials. It remains a great challenge to generate superhydrophobic surfaces with tunable adhesion using a rapid, facile, and simple fabrication process.

Recently, micromachining for fabricating superhydrophobic surfaces by a femtosecond laser has attracted much interest because it can not only produce the topography with two scale roughness but also be applied to a wide variety of materials.^{35–41} Controlled by a computer, complex structures or patterns can be realized, exhibiting unique wetting property. Mazur et al.³⁵ and Stratakis et al.³⁶ obtained excellent superhydrophobic Si surface by femtosecond laser irradiation under a reactive gas (SF_6) atmosphere. The surface showed a periodic lotus-leaf-like conical spikes structure. In our previous investigation, we fabricated a new superhydrophobic surface with hierarchical mesh-porous structure by a femtosecond laser on silicon in an ambient environment.^{37'} The surface showed ultralow water adhesion. On this basis, the anisotropic wetting was realized by restricting a droplet on an unstructured Si hydrophobic domain between two superhydrophobic strips.³⁸ Then the volume-induced wetting transition between anisotropic and isotropic was achieved on directional structures which are composed of periodical hydrophobic flat triangular pattern and superhydrophobic domain.³⁹ In addition, the superhydrophobic surfaces with microwell array structures were rapidly produced on polydimethylsiloxane (PDMS) films by a point-by-point femtosecond laser scanning process.^{40,41} By adjusting the extent of overlap of the adjacent microwells, the adhesion could be tuned from ultralow to ultrahigh.

In this paper, we will demonstrate a simple way to realize superhydrophobic patterned PDMS surfaces with tunable adhesion by a femtosecond laser. These surfaces are composed of superhydrophobic laser-induced structures and hydrophobic unstructured square array. The as-prepared surfaces show superhydrophobicity, and the adhesion of these surfaces can be tuned from ultralow to ultrahigh by adjusting the length of the side of unstructured square. In addition, controllable droplet rebound behavior, droplet fast stop, and small water droplet transfer are investigated by as-prepared surfaces.

2. METHOD AND EXPERIMENTAL SECTION

2.1. Material. Polydimethylsiloxane (PDMS) is an intrinsic hydrophobic material, widely used in biomedicine field and labon-chip devices. The solid PDMS film was obtained by using a 10:1 mixture by weigh of PDMS prepolymer/curing agent (Dow Corning Corporation). And then the mixture was poured onto the clean glass plates and kept there for 10 min in a vacuum desiccator, so that the trapped air bubbles could emerge to the surface. After removing all the air bubbles, the mixture was cured at 100 °C for 2 h in an oven. The thickness of the PDMS samples was about 1 mm.

2.2. Surface Laser Irradiation. The schematic of experimental setup is shown in Figure 1a. The PDMS samples were mounted on a motorized *x-y-z* translation stage controlled by a computer and positioned perpendicularly to the direction of laser incidence and then irradiated by a 50 fs regenerative amplified Ti:sapphire laser system at the center wavelength of 800 nm with a repetition rate of 1 kHz. The laser beam was focused on PDMS surface with a microscope objective lens $(10\times, NA = 0.30, Nikon)$ on the front side of the sample. A mechanical shutter was used as a switch to turn on and off the laser beam. Following the irradiation process, the samples were cleaned by acetone, alcohol, and deionized water in an ultrasonic bath at room temperature for 10 min each time.

2.3. Structured Square Array. Figure 1b shows a schematic illustration of the configuration used to fabricate square array pattern on PDMS films. The line-by-line scanning method is employed to fabricate this pattern. The light blue line denotes the scanning route. Each sample was fabricated at a scanning speed of 5 mm/s, and the interval of adjacent laser scanning lines was held constant at 5 μ m. The laser energy is 30 mW. According to our previous work, the adjacent laser-pulse-induced craters were strong overlapping during the scan, resulting in a homogeneous rough structure.⁴⁰ After femto-second laser irradiation, the unstructured domain turns out to be a square array pattern (the white domain). In view of the size of water droplet and machining precision, the period (*T*) of the square array was set at 200 μ m (*T* \equiv 200 μ m). By adjusting



Figure 2. (a) SEM image of as-prepared square array patterns. (b) Large magnification SEM image of the structure irradiated by a femtosecond laser.

the length (L) of the side of unstructured square, the size and shape of the square array can be modulated as well as the wettability.

2.4. Morphology Analysis and Contact Angle Characterization. The morphology of the as-prepared surfaces irradiated by a femtosecond laser was observed by a JSM-7000F scanning electron microscope (SEM, JEOL, Japan). The water contact angles and sliding angles of 7 μ L water droplets on the surfaces were measured by a JC2000D4 contact-angle system (POWEREACH, China) at ambient temperature, using a sessile drop method. The average values were obtained by measuring five different points on the same surface.

3. RESULTS AND DISCUSSION

Figure 2a shows the SEM image of the as-prepared PDMS surface consisting of periodic square array. Further magnified SEM image shows that the femtosecond laser scanned domain is characterized by an irregular three-dimensional rough structure of an order of micrometer decorating with tens or hundreds of nanometers nanostructures (Figure 2b). The value of static CA on the entire laser-induced surface $(L = 0 \ \mu m)$ is as high as $162 \pm 1^{\circ}$ (Figure 3b), even without any modification by materials of low surface energy. The droplet will easily roll off when the entire rough surface is tilted 1°, showing an ultralow water adhesion (Supporting Information, Movie S1). The ultralow adhesive superhydrophobicity can be explained by Cassie's theory.^{37,42} The water droplet is suspended by the gas layer trapped at the micro- and nanoscale structures. The contact area between the surface and the droplet is so small that the droplet almost has no wetting of the space between the rough structures. The nonirradiated domain is flat PDMS and shows intrinsic ordinary hydrophobicity with a water CA of 110 \pm 1°. Therefore, the as-prepared square array patterns are heterogeneous topographic surfaces including both superhydrophobic and ordinary hydrophobic domains.

The length (L) of the side of unstructured square, which is the most crucial structure parameter, has an important effect on the water CA and SA of the as-prepared surfaces. Figure 3a shows the relationships between L and the CA/SA. When L is no more than 180 μ m, the as-prepared surfaces show superhydrophobicity with water CAs being larger than 150°. For example, the top half images of Figure 3b–e show the shapes of a water droplet on the as-prepared surfaces with a





Figure 3. (a) Relationships between the length (*L*) of the side of unstructured square and the CA (left)/SA (right). (b–e) Static properties and dynamic behaviors of droplets on the as-prepared square arrays with different *L*: (b) $L = 0 \ \mu m$, (c) $L = 140 \ \mu m$, (d) $L = 170 \ \mu m$, and (e) $L = 180 \ \mu m$. The $L = 0 \ \mu m$ means that the entire surface is irradiated by a femtosecond laser. The curved arrows in (b– e) indicate the droplets' rolling direction and state on the tiled surfaces.

water CA of $162 \pm 1^{\circ} (L = 0 \ \mu m)$, $155.9 \pm 1.5^{\circ} (L = 140 \ \mu m)$, $152.7 \pm 1^{\circ} (L = 170 \ \mu m)$, and $150 \pm 2^{\circ} (L = 180 \ \mu m)$. While when the *L* is larger than $180 \ \mu m$, the CA sharply decreases from 150° to 110° , which is the intrinsic CA of hydrophobic PDMS. The water adhesion, which is an important property of a solid surface, can be accurately assessed by the sliding behavior of a water droplet. As to that of the SA, it increases slowly at first and the water droplet can move very easily when the surfaces are only slightly tilted (Figure 3b) or shaken when *L* is no more than 140 μ m (Movie S1). However, with the *L* increasing from 140 to 180 μ m, the SA on the as-prepared surfaces abruptly increases from $10 \pm 1.5^{\circ}$ to $54 \pm 3^{\circ}$ and then

to 90° that the water droplet does not slide down even when the as-prepared surface is vertical or turned upside down (Figure 3c–e and Movies S2–S4). Finally, the water droplet is firmly pinned on the as-prepared surfaces without any movement at any tilted angles when L is greater than 180 μ m.

It is worth noting that all the CAs near the SA variable region are larger than 150°. This result implies that there is a transition between the superhydrophobic surface with ultralow adhesion and the superhydrophobic surface with ultraling adhesion for the as-prepared square arrays. The superhydrophobic surfaces with ultralow adhesion can be obtained in a wide range of *L* from 0 to 140 μ m (region I in Figure 3a). Conversely, the superhydrophobic/hydrophobic surfaces with ultrahigh adhesion can be obtained at $L \ge 180 \ \mu$ m (region III in Figure 3a). In the range of *L* from 140 to 180 μ m, the adhesion can be tuned from ultralow to ultrahigh (region II in Figure 3a).

The modulation of the wettability and adhesion of these surfaces can be ascribed to the change in the area fraction of laser structured and nonstructured domains. Based on the above, the femtosecond laser structured domain shows superhydrophobicity with ultralow water adhesion. Accordingly, the droplet on the laser-irradiated surface is the Cassie state.⁴² The water only contacts the peak of the micro/ nanoscale hierarchical surface, leading an extremely discontinuous three-phase contact line (TCL). On the contrary, the droplet will completely wet the nonirradiated flat surface and form a continuous TCL. This contact model can be considered as the Young or Wenzel state.^{17,31} As a result, the nonstructured flat PDMS shows ordinary hydrophobicity with ultrahigh water adhesion because large contact area results in more van der Waals force. Therefore, a water droplet on the heterogeneous as-prepared surfaces generally composes of both Cassie and Young contact state, as shown in Figure 4. With the



Figure 4. Contact model of water droplet on a heterogeneous topographic surface including both micro/nanoscale rough structures and flat domain.

L increasing, the area fraction of the laser structured domain as well as the Cassie contact will decrease, resulting in a decline of CA. On the contrary, the area fraction of the nonstructured domain as well as the Young contact will increase, endowing the water adhesion or SA increase.

The length of the side of unstructured square can greatly influence droplet impact on the as-prepared surfaces, and the droplet rebound behavior can be tuned. Snapshots in Figure 5 show the rebound behaviors of 13 μ L water droplets on the as-prepared square arrays with L = 0, 140, 170, and 180 μ m (Movies S5–S8). The water droplets are all released from a syringe with a height of 5 mm from the needle tip to the surfaces. When L increases from 0 to 140 μ m, the droplet can bounce numerous times (Figure Sa,b). The droplet would

deform into a flat ellipsoid once it contacted the as-prepared and then recovered quickly. Next it rebounded off the surface. It can be seen that the shape of the droplet changes observably during impact because its kinetic energy transforms into internal energy and vibration energy due to surface deformation. However, as L increases, the droplet will be harder to rebound. The droplet takes 116.2 ms to touch the asprepared surface with L of 0 μ m a third time, which is more than 99.6 ms for the as-prepared surface with L of 140 μ m. When L reaches values of 170 and 180 μ m, the droplet sticked to the surface (Figure 5c,d). At $L = 170 \ \mu m$, the droplet contacted a small area with the sample and almost rose up off at t = 41.5 ms. However, the droplet pressed against the upper surface of the sample at $L = 180 \ \mu m$, showing a higher water adhesion. The results indicate that the rebound behavior can be apparently tuned by varying the length of the side of unstructured square, from numerous rebound at small L to a nonrebound at large L with droplet sticking to the surface. The controllable rebound behavior may have applications in selfcleaning, inkjet printing, and spraying techniques.^{16,43}

Figure 6 shows the process of a water droplet rolling on the surface consisting of two neighboring square arrays with L = 40 and 170 μ m. The front part shows ultralow water adhesion, and the rear part has strong water adhesion. When the sample was tilted a little, the water droplet will roll off freely on the front part of the surface like that of a water droplet on a lotus leaf. The velocity of the droplet was sharply reduced when it gets to the rear part of the surface (Movie S9). Its kinetic energy transformed into stored energy, which is shown in the form of sharply change of the shape of the water droplet. Finally, the water droplet was pinned on the surface motionlessly. This phenomenon may be utilized to solid transfer and control of droplet movement.^{16,33,34}

The superhydrophobic surface with ultrahigh adhesion can be used as a "mechanical hand" to transfer small water droplets from a superhydrophobic surface to an ordinary hydrophobic surface (Movie S10). As seen in Figure 7, a water droplet was first placed on a superhydrophobic surface (surface of A) with ultralow water adhesion (step 1). Then, the superhydrophobic surface (surface of B) with ultrahigh adhesion was lowered down to contact the water droplet (step 2). And the water droplet was completely adhered to the B-surface due to the stronger water adhesive force. The water droplet was completely transferred from A surface to B surface after lifting the B surface up (step 3). Next, the B surface was moved to another location above a hydrophobic surface (surface of C) with higher water adhesion (step 4). And the B surface was lowered down again until the hanging droplet contacted the C surface (step 5). Finally, lifting the B surface up, the water droplet was detached from the B surface and transferred to the C surface (step 6). In this way, the water droplet was moved from the A surface to C surface. Generally, a water droplet on a superhydrophobic surface usually takes a quasi-spherical shape, which dramatically reduces the contact area between the liquid and the solid. Therefore, the transfer process almost has no loss of microdroplet for a small contact area. Moreover, such transport process could be repeated a large number of times for the stability of PDMS. The droplet transfer ability of superhydrophobic surface with ultrahigh adhesion has some wider applications such as drug delivery and component siteoriented release.18-20

t=0ms

t=8.3ms

t=16.6ms

t=24.9ms



Figure 5. Time sequences of snapshots of a 13 μ L water droplet free-falling and impacting the as-prepared square arrays with different *L*: (a) *L* = 0 μ m, (b) *L* = 140 μ m, (c) *L* = 170 μ m, and (d) *L* = 180 μ m.



Figure 6. The process of a 7 μ L water droplet rolling on the surface consisting of two neighboring square arrays with different *L*. The front part: *L* = 40 μ m; the rear part: *L* = 170 μ m. The curved arrows indicate the droplet's state of motion.



Figure 7. Process of transferring a 7 μ L water droplet from the A surface to C surface using the B surface. Surfaces of A, B, and C were as-prepared square arrays with L of 0, 180, and 190 μ m, respectively.

4. CONCLUSIONS

In conclusion, superhydrophobic patterned PDMS surfaces with tunable water adhesion that ranges from ultralow to ultrahigh have been prepared by a femtosecond laser. These surfaces are composed of superhydrophobic laser-induced structures and hydrophobic unstructured square array. By varying the length of the side of unstructured square, the wettability and adhesion of these films can be tuned. The modulation of the wettability and adhesion of these surfaces is ascribed to the change in the area fraction of laser structured and nonstructured domains. Controllable droplet rebound behavior, droplet fast stop, and small water droplet transfer are achieved by as-prepared surfaces. We believe that the developed approach in tuning the adhesion of the superhydrophobic surfaces by this simple method will have important potential application in the manipulation of water droplets/fluid.

ASSOCIATED CONTENT

S Supporting Information

Movies S1–S10. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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