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A bioinspired planar superhydrophobic microboat

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Abstract
In nature, a frog can easily rest on a lotus leaf even though the frog’s weight is several times the weight of the lotus leaf. Inspired by the lotus leaf, we fabricated a planar superhydrophobic microboat (SMB) with a superhydrophobic upper surface on a PDMS sheet which was irradiated by a focused femtosecond laser. The SMB can not only float effortlessly over the water surface but can also hold up some heavy objects, exhibiting an excellent loading capacity. The water surface is curved near the edge of the upper surface and the SMB’s upper edge is below the water level, greatly enhancing the displacement. Experimental results and theoretical analysis demonstrate that the superhydrophobicity on the edge of the upper surface is responsible for the SMB’s large loading capacity. Here, we call it the ‘superhydrophobic edge effect’.

Keywords: Planar microboat, superhydrophobic edge effect, loading capacity

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, superhydrophobic microboats (SMBs) and their analogues have attracted intensive attention because of their important role in aquatic devices and potential applications in autonomous devices sensing pollution on water or as the support feet of aquatic microrobots [1–6]. In nature, a frog can easily rest on a lotus leaf, even though it is heavier than the lotus leaf, as illustrated in figure 1(a). It is well known that the upper surface of the lotus leaf comprises microscale papillae decorated with nanometer-sized branch-like protrusions (figures 1(b), (c)) [7–9]. In addition, the papillose epidermal cells on the surface of a lotus leaf are covered with a layer of epicuticular hydrophobic wax crystals. The coexistence of the hierarchical structure and the chemical layer reduces the contact area between a water droplet and its underlying surface, resulting in a remarkable superhydrophobicity with a contact angle (CA) of 153° ± 1° [10–14]. Unlike to the upper surface, the lower surface of the lotus leaf shows weak hydrophobicity (CA = 135° ± 2°), despite it also having a micro/nanoscale hierarchical structure (figures 1(d), (e)). This could be attributed to the relatively low height and sparsity of the microstructures. An interesting question to consider is which surface of a lotus leaf will enhance its loading capacity. It has never been discussed before.

Up to now, several microboats have been fabricated by biomimetic manufacturing technologies [15–23]. Inspired by water striders staying and walking on the water surface [24–26], a kind of miniature microrobot has been realized [5, 6, 21–23]. The body of the microrobot can be suspended on the water by many superhydrophobic supporting fine wires, which are similar to the water strider’s legs, because they can make the water surface curve and the surface tension force is significantly enhanced. Although the microrobot can support a weight several times heavier than its body, the long legs make its body length more than 10 cm, which occupies a large area of the water’s surface, and the water’s surface was not fully used because the legs have to be separated by a certain distance [22]. Compared to the strider-like microboat, the leaf-like microboats are more compact and can totally use the water surface. Pan et al reported a miniature boat fabricated by superhydrophobic copper meshes [15], which exhibited...
Figure 1. (a) Photo of a frog resting on a lotus leaf. (b), (c) SEM images of the upper surface of a lotus leaf. The inset shows the shape of a 5 μl water droplet on that surface with a water CA of 153° ± 1°. (d), (e) SEM images of the lower surface of a lotus leaf. The inset shows the shape of a 5 μl water droplet on that surface with a water CA of 135° ± 2°.

They believed the large loading capacity arose from the air film of 1.5 mm surrounding the superhydrophobic surfaces of the boats. Under the influence of this article, a series of SMBs were fabricated [4, 16, 17]. The heavy loading property of those microboats was explained by the air films. In fact, an air-film thickness of several millimeters seems unlikely because the microstructure of the superhydrophobic surface is only microscale or nanoscale. An in-depth exploration of the mechanism of the heavy loading property of the planar microboats is still important to the development of biomimetic materials for aquatic applications.

In this paper, inspired by the lotus leaf, we report a planar SMB fabricated by a femtosecond laser. The SMB has a superhydrophobic upper surface and exhibits a remarkable loading capacity. To reveal the underlying mechanism of the SMB’s loading capacity, five types of planar microboats are designed and studied on a comparative basis. Experimental results and theoretical analysis demonstrate that the superhydrophobicity of the upper surface of the SMB, especially the superhydrophobicity of the edge of the upper surface, is responsible for the SMB’s large loading capacity on the water surface. This effect is hereby dubbed the ‘superhydrophobic edge effect’. Our study clarifies the buoyancy generation mechanism of planar SMB, and provides a novel concept for the design and manufacturing of super-buoyancy aquatic devices.
Figure 2. (a) SEM image of the PDMS surface irradiated by a femtosecond laser. The top-right inset shows a droplet on the superhydrophobic PDMS surface with a water CA of 156° ± 2°. (b)–(d) Optical images of an SMB floating on the water surface: (b) top view; (c) side view; (d) cross-section view. The yellow dotted line shows the boundary of air and water.

2. Experimental details

Polydimethylsiloxane (PDMS) sheets are intrinsically hydrophobic materials (CA = 110°), which were generally prepared from a 10:1 mixture (by weight) of prepolymer (DC-184A, Dow Corning Corporation) and curing agent (DC-184B, Dow Corning Corporation), poured onto a clean glass plate and kept there for 10 min in a vacuum desiccator, so that the trapped air bubbles could emerge to the surface. After removing all of the air bubbles, the mixture was solidified in an oven at 120°C for 2.5 h. The solidified PDMS sample was carefully peeled off the glass plates. The thickness of the sample was about 0.73 mm and the density was about 1.025 g cm⁻³, which made the fluctuation of thickness of the SMB have little effect on its loading capacity. Then the sample was cut into a wafer with the diameter of 4 cm.

The method of forming a superhydrophobic surface was to irradiate the PDMS sheet by a regenerative amplified Ti:sapphire laser system (center wavelength: 800 nm; pulse duration: 50 fs; repetition: 1 kHz). The details of experimental setup and the scanning method are given in our previous work [27–32]. The Gaussian laser beam was focused by a microscope objective lens (10×, NA = 0.30, Nikon) on the front side of the sample with laser power of 30 mW. The samples were fabricated at scanning speed of 5 mm s⁻¹ and the interval of adjacent laser scanning lines was held constant at 5 μm. Following the irradiation process, the samples were cleaned by deionized water in an ultrasonic bath at room temperature for 10 min. In the experiment, a hydrophilic surface was used as a comparison sample because the big difference between superhydrophobicity and hydrophilicity would produce obvious comparison results. The way we formed a hydrophilic surface was to cover a hydrophilic (the intrinsic water CA is 73°) thin film of sticky tape (Ha Bagou, China) on the PDMS wafer. The density of the sticky tape was about 0.915 g cm⁻³. The thickness of the hydrophilic films was about 0.03 mm, which was negligible compared to the PDMS sheet.

Fresh lotus leaves were obtained at the South Lake Park in Xi’an, China. The upper and lower surfaces of the lotus leaf were observed by a Quanta 250 FEG scanning electron microscope (FEI, Holland) in a low vacuum environment. The morphology of the as-prepared surfaces irradiated by a femtosecond laser was characterized by a JSM-7000F scanning electron microscope (JEOL, Japan). The water contact angles and the sliding angles (SAs) on the as-prepared surface were measured by a JC2000D4 contact-angle system (POWEREACH, China) at ambient temperature, using a sessile drop method. The loading capacity of the planar microboats was investigated by carefully adding weights (from 10 mg to 1 g) until the microboats submerged. The loading capacity of the SMB equals the weight of the loads at this time. The measured values were less than the real values for some operational reasons. To reduce the measurement error, all values of loading capacity were measured five times and the maximum value was chosen.

3. Results and discussion

Figure 2(a) shows the scanning electron microscopy (SEM) image of the upper surface of the fabricated SMB, which was entirely irradiated by the femtosecond laser. The upper surface is composed of many microscale undulant outthrusts. The further-magnified SEM image shows that many irregular nanoparticles, with an average diameter of several hundred nanometers, are distributed randomly on the outthrusts (bottom-right inset of figure 2(a)). The micro/nanometer binary structure can trap a large amount of air, which results in the superhydrophobicity of the sample surface. The top-right inset of figure 2(a) shows an image of an 8 μl water droplet lying on the upper surface of the SMB. The static CA on the as-prepared surface is 156° ± 2° and the SA is lower than 4°. Both the high CA and the low SA demonstrate that the femtosecond laser-induced dual-scale hierarchical structure enhanced the hydrophobicity of the surface. The lower surface of the SMB
Figure 3. Selected frames of the as-prepared SMB submerging into water. The SMB was released under the water surface. The yellow arrows indicate the location of the SMB.

Figure 4. Schematic diagram of the design of different microboats. The flat PDMS shows intrinsic ordinary hydrophobicity. The micro/nanoscale hierarchical structure shows superhydrophobicity. The hydrophilic thin film shows ordinary hydrophilicity.

sample is not processed and shows intrinsic hydrophobicity. Therefore, the upper superhydrophobic surface of the SMB in combination with the lower hydrophobic surface is very similar to that of a lotus leaf.

To investigate the SMB’s floating behavior, the SMB was put on the water surface and weights were carefully loaded onto it, as shown in figure 2(b). The SMB could easily carry the loaded weights, which were much heavier than itself on the water surface, exhibiting an excellent loading capacity. Interestingly, the SMB made the water surface curve, and kept floating even if its upper surface was below the water surface, as shown in figures 2(c), (d). The formation of the side convex water surface (the yellow dotted line in the inset of figure 2(d)) was caused by the surface tension of water and the superhydrophobicity of the sample surface. This floating phenomenon is very similar to that seen in the lotus leaf (figure 1(a)). The total displacement is greatly increased, as is the loading capacity. The SMB capsized when the loads were over 5.58 g in this case, which exceeds the maximum buoyancy force estimated from the weight of water with the same volume of the SMB (i.e., 0.92 g). However, the as-prepared SMB will submerge into water if it is released under the water surface, as shown in figure 3. This indicated that the buoyancy force is not enough to float it. If the air-film hypothesis is correct, the SMB should be able to get out of water [15–17]. Based on this fact, we believe that the precise internal mechanism of the large loading capacity of the planar SMBs may not be as previously thought.

The loading capacity of different types of planar microboats is compared with each other to determine the origin of the large buoyancy of SMB. As shown in figure 4, three different types (type-1–type-3) of microboats were designed. Type-1 served as a comparison. It was treated by covering hydrophilic thin films (with an intrinsic water CA of 73°) on
both upper and lower surfaces. Using hydrophilic surfaces is to produce significant comparison results. Type-2 and type-3 are actually the same, composed of a superhydrophobic surface and a hydrophilic surface, but lying different ways. For type-2, the superhydrophobic surface faces down and the hydrophilic surface faces up; for type-3, the hydrophilic surface faces down and the superhydrophobic surface faces up. The loading capacity of the type-1 to type-3 microboats were measured and the results are shown in figure 5. Within the range of error permitted, the loading capacity of type-2 is basically equal to that of type-1, which shows that the lower superhydrophobic surface of the microboat will not influence the loading capacity. The loading capacity of the type-3 microboat is 5.58 g, which increased by 41.62% compared to type-1 and type-2, demonstrating that the superhydrophobicity of the upper surface plays the key role in enhancing the loading capacity of SMBs.

Interestingly, it was found that water would rush to the center of the upper surface in an instant when the water surface was curved a certain degree, resulting in the microboat turning over. It seems that the superhydrophobicity on the edge of the upper surface, rather than at the central part, will determine the loading capacity of the SMB. To demonstrate this, type-4 and type-5 microboats were fabricated, as shown in figure 4. Only the edge of the PDMS wafers were treated by the femtosecond laser, forming 1.5-mm-wide superhydrophobic ring edges and original PDMS centers. The other sides were covered by the hydrophilic thin films. The hydrophilic surface was face up for the type-4 and face down for type-5. The loading capacities of the two types of microboats are shown in figure 5. The loading capacity of type-4 increased about 3.55% compared to type-1, which shows almost the same loading capacity as type-1 and type-2. This is consistent with the conclusion above because the upper surfaces of the three types of microboats are same. For the type-5 microboat, the loading weight was 5.56 g, which indicates that the loading capacity of the type-5 microboat is very close to that of the type-3 microboat. It has been proved that the wettability of solid surfaces is mainly determined by the water–solid contact lines [32–36]. In addition, the water will not contact the central part of the microboats when they float on the water surface, and the buoyancy force of the SMB mainly resulted from the superhydrophobicity on the edge of the upper surface. Hence, we call it the ‘superhydrophobic edge effect’.

Figure 6 schematically displays the sinking process of an SMB by increasing the loading weights on it. Figure 6(a) shows the moment when the SMB just contacts the water surface, and the three-phase contact line (TCL) is on the lower surface of the microboat. After releasing the SMB without any load, because of its own weight, the SMB will sink into the water and the buoyancy force will increase at the same time. When the SMB reaches a balance where the buoyancy force equals its own weight, the water surface would be bent into a curved profile because of the surface tension. The bending angle at the TCL is \( \varphi \), and the distance between the TCL and water surface is \( h_0 \), as shown in figure 6(b). When loaded by some weights, the SMB will continue to sink. The TCL goes down and \( h_0 \) increases. Consequently, \( \varphi \) reaches about 20° (figure 6(c)), which is the upper limit of the water bending angle because the maximum CA between the water and original PDMS (the sidewall of the SMB) is only about 110°. By adding the loads, the TCL raises and \( \varphi \) remains constant (figure 6(d)) until the TCL contacts with superhydrophobic upper surface of the microboat, as shown in figure 6(e). On the upper surface, the CA will be increased significantly due to the laser-induced superhydrophobicity, and \( \varphi \) will also be increased. This enables us to load more weights, even though the water surface is beyond the upper surface of the microboat. The value of \( \varphi \) can even be larger than 90° (figure 6(f)), which is the boundary between the hydrophilicity and the hydrophobicity. Finally, \( \varphi \) reaches the maximum, which is considerably larger than 90°, as shown in figure 7. Meanwhile, the height (\( h_0 \)) from the TCL to the horizontal water surface also achieves the highest value. If we add a tiny bit more load, the water will flow over the upper surface and the SMB will be completely submerged. In this case, the weight of the load is the maximum value. And the loading capacity of the SMB equals the weight of the load at this time.

To analyze the loading capacity of the SMB, dynamic analysis is brought out for the interaction forces between the SMB and water. As shown in figure 7, the lifting forces exerted on the SMB include: (1) surface tension (\( F_\alpha \)), and (2) the buoyancy force (\( F_b \)) that acts on the bottom of the boat. Then the total lifting force exerted on a SMB can be described by [38–40]:

\[
F = F_\alpha \sin \varphi + F_b
\]  

(1)

where

\[
F_\alpha = 2\pi \alpha r
\]

and \( \alpha \) is the surface tension coefficient, \( r \) is the radius of the circular microboat, \( \rho \) is the density of water, \( g \) is the gravitational constant, \( z \) is the thickness of the SMB, \( h_0 \) is the distance from the horizontal surface to the TCL (\( h_0 \approx 2\sqrt{k}\sin\frac{\varphi}{2}, k = \alpha/\rho g \)) [6, 37] and \( S \) is the surface tension of the water.
Figure 6. The theoretical sinking process of an SMB when loads are carefully added to it.

Figure 7. Cross-sectional model describing the air–water interface of an SMB when it reaches the maximal loading capacity. The key is the same as in figure 6. The yellow dotted line is copied from the inset of figure 2, depicting the real curved water surface.

area of the lower surface of the SMB. Then equation (1) is becomes

$$ F \approx 2\pi ar \sin \varphi + \rho g \left( z + 2\sqrt{k} \sin \frac{\varphi}{2} \right) S. \tag{2} $$

Interestingly, for the water striders, the lifting force comes mainly from the surface tension because their legs are extremely thin. The $F_b$ can be neglected due to the small surface area, $S$. Whereas, for the planar microboats in this paper, with perimeters $2\pi r \ll 1$ m, $F_o$ is negligible compared to $F_b$. So the main source of the lifting force of the planar microboats is very different from that of the line-like microbots. Here, $F$ can be approximately written as

$$ F \approx F_b \approx \rho g \left( z + 2\sqrt{k} \sin \frac{\varphi}{2} \right) S. \tag{3} $$

A large CA results in a large $\varphi$ because both of them denote for the surface wettability of water. Therefore, the equation (3) shows that the total lifting force exerted on the SMB is positively related to the thickness, the water CA of the upper surface and the surface area of lower surface of the microbot. This is in good agreement with the above experimental results. The higher the hydrophobicity of the upper surface of the planar microbots, the larger the loading capacity that can be obtained. Superhydrophobicity of the upper surface of the SMB can endow a large-enough $\varphi$ and improve the SMB’s loading capacity greatly. In fact, the first term $\rho g z S$ is the gravity of water with the same volume of the SMB, and the last term $2\rho g \sqrt{k} \sin \frac{\varphi}{2}$ is the extra force ($F_e$) due to the curved water surface at the edge of the SMB’s upper surface which is below the water surface. So the extra force per unit area equals $2\rho g \sqrt{k} \sin \frac{\varphi}{2}$, which is positively related to the $\varphi$ or the CA. It shows that the extra force per unit area of the planar SMB is larger than those water-strider-inspired aquatic devices, indicating a higher utilization of the water surface [5, 25]. For an ordinary boat whose thickness, $z$, is commonly large, the $F_e$ can be ignored because it is too small compared to $\rho g z S$. But for the leaf-like microboat, the $F_e$ becomes the primary contributor to the loading capacity. In an extreme case, when the thickness of the SMB approaches to zero ($z \to 0$), the loading capacity is mainly caused by the wettability of the upper surface and its bottom surface area ($F \to 2\rho g \sqrt{k} \sin \frac{\varphi}{2}$).

In nature, animals and plants have adapted to specific environments through many generations of evolutionary changes. Our experiment shows that, for a lotus leaf, the superhydrophobicity of the upper surface is not only for the well-known self-cleaning effect which can keep the leaf surface clean [7], but also to enhance its loading capacity, which enables it to float on the water surface even though some animals such as frogs rest on it. Both effects will benefit its growth by allowing it to receive more sunlight and maximize photosynthesis. Our experimental result can also be used to improve the floating capacity of an object. For example, a waxed metal coin can float on water, as shown in figure 8, even though the density of metal is much higher than water. This phenomenon can be explained by the similar principle of the SMB. The wax layer changes the surface condition of the coin from hydrophilicity to hydrophobicity, and the bent water provides an extra force to float the coin.
4. Conclusions

In this paper, inspired by a lotus leaf, we presented a planar superhydrophobic microboat (SMB) by the femtosecond laser surface structuring process. By fabricating a superhydrophobic upper surface with the femtosecond laser, the loading capacity of the PDMS wafer was greatly increased. Experimental results and theoretical analysis demonstrate that the superhydrophobicity of the upper surface of the SMB, especially the superhydrophobicity of the edge of the upper surface, is responsible for the SMB’s large loading capability on the water surface. The buoyancy force is larger than the gravity of water with the same volume of the SMB because the superhydrophobic upper surface on the edge of the SMB can bend the water and enable the SMB's upper edge below the water surface. The total displacement is greatly increased, as well as the buoyancy force. Our finding provides an in-depth understanding of the superhydrophobic effects in natural species such as the lotus leaf, and opens up a new route to fabricate bioinspired aquatic devices such as SMBs.

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