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Research Article

Bionic Duplication of Fresh *Navodon septentrionalis* Fish Surface Structures

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Biomimetic superhydrophobic surface was fabricated by replicating topography of the fresh fish skin surface of *Navodon septentrionalis* with polydimethylsiloxane (PDMS) elastomer. A two-step replicating method was developed to make the surface structure of the fresh fish skin be replicated with high fidelity. After duplication, it was found that the static contact angle of the replica was as large as 173°. Theoretic analysis based on Young's and Cassie-Baxter (C-B) model was performed to explain the relationship between structure and hydrophobicity.

1. Introduction

Biological organisms with superhydrophobic surfaces always give human inspiration to design and create novel antifouling and self-cleaning interfacial materials. Water contact angles on these superhydrophobic surfaces can be greater than 150° [1, 2]. Previous studies showed that these organisms generally have textured surfaces with hierarchical structure in micrometer and nanometer order [3, 4]. These textured superhydrophobic surfaces gained many attentions in recent years. Rough surface structures of some terrestrial organisms such as lotus leaves, paddy leaves, and roseleaves were replicated by template technique [5–8].

Actually in nature, not only terrestrial organisms but some fishes in water also have textured superhydrophobic surfaces. *Navodon septentrionalis* is one of typical fish covered with bony scale [9–11]. The skin surface of *Navodon septentrionalis* is as rough as sandpaper. However, compared with other organisms, the surface of fresh fish is humid with water. The fatal thing is that the soft and deformable materials cannot be completely wetted by the liquid used for replication. As a result, the surface structure cannot be replicated faithfully.

Therefore, in this paper, we developed a two-step replication method for the duplication of fresh fish surfaces. The surface structure was replicated with high fidelity by this method. Scanning electron microscopy (SEM) and optical microscope were employed to investigate the morphology and structures. Static contact angle of reproduction was studied and analyzed by a circle-square model using Cassie-Baxter (C-B) theories.

2. Materials and Methods

Template technique was one of the soft lithography techniques. Firstly, a liquid was used to cast on the template surface. After solidification, the template was removed and the inversive structures were transferred to the solidified material. With the negative template, positive structure templates were obtained by a second replication. In our experiment, a piece of fresh *Navodon septentrionalis* fish skin was cut, washed, and fixed on a slide. Polyvinyl alcohol (PVA) was dissolved in water to 18% (w/w_0). The process to duplicate fish surface structure is shown in Figure 1, which contains two main steps. First, PVA water solution was cast on the fish skin (original template). When water in the solution was evaporated at room temperature after 24 h, the sample was heated to 50°C for 4 h in oven. A layer of PVA (negative template) formed after the treatment. Subsequently, PVA layer was peeled off gently. Second, a mixture of liquid PDMS monomer and its catalyzer was cast on the negative PVA template. The proportion of weight of

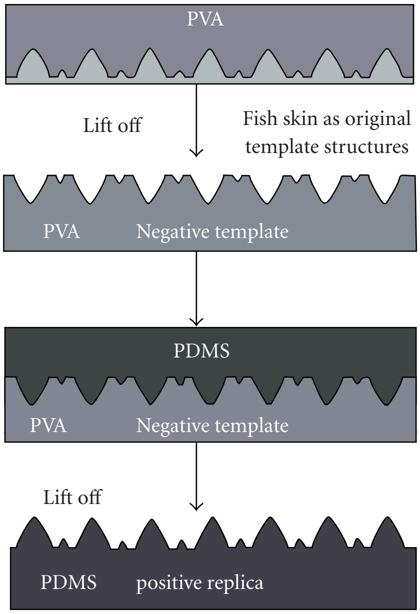


Figure 1: Illustration of the fish surface structure duplication process.

PDMS monomer and its catalyzer was controlled between 11 : 1 and 16 : 1. The reaction was carried out at 80°C for 15 min. After PDMS was solidified, it was peeled off carefully. By this method, complex patterns of the fresh fish surface were transferred to the solid-state PDMS with high fidelity.

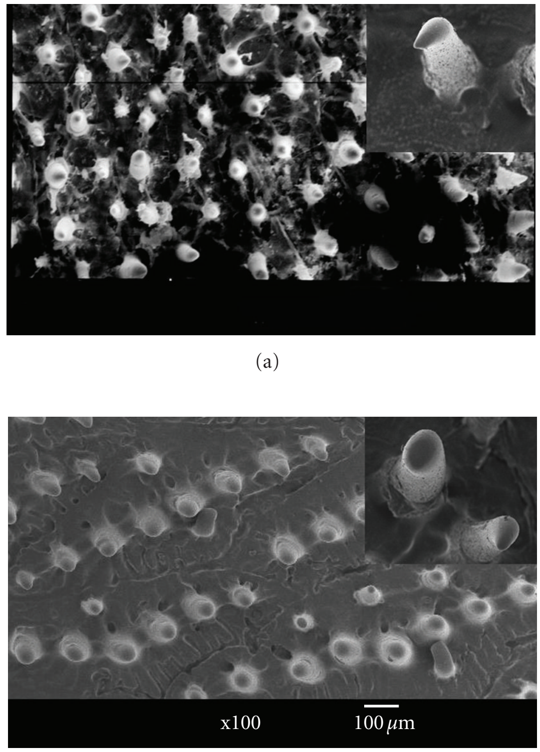
The morphology of fish surface (original template) and positive replica was characterized by SEM (Hitachi S-3000N) and optical microscope (Olympus IX51). A sessile drops method (Zhong-chen JC2000C1) was used to measure static contact angles of water droplets on PDMS replicas.

3. Result and Discussion

SEM images of *Navodon septentrionalis* fish and PDMS replicas are shown in Figure 2. Rows of ordered awls with distance about 100 μm can be observed. The diameters of awls at bottom and top side are about 40 μm and 10 μm, respectively. Between the awls sophisticated wrinkle structures in micro and nanoorder were observed. These complex structures were well replicated to the PDMS surface. From Figures 2(a) and 2(b), original template and duplicate have both intricate surface morphology and scales. These results indicated that the surface structure of fish skin had been transferred to PDMS replicas. In addition, the negative template (PVA mould) can be used for many times for replication.

Figure 3 shows water drops (5 μL) on textured positive replicas (Figure 3(a)) and flat sheet (Figure 3(b)), both of which were made of PDMS without any chemical modification. The contact angle of the positive replica is 173° while it is 100° for the flat PDMS sheet.

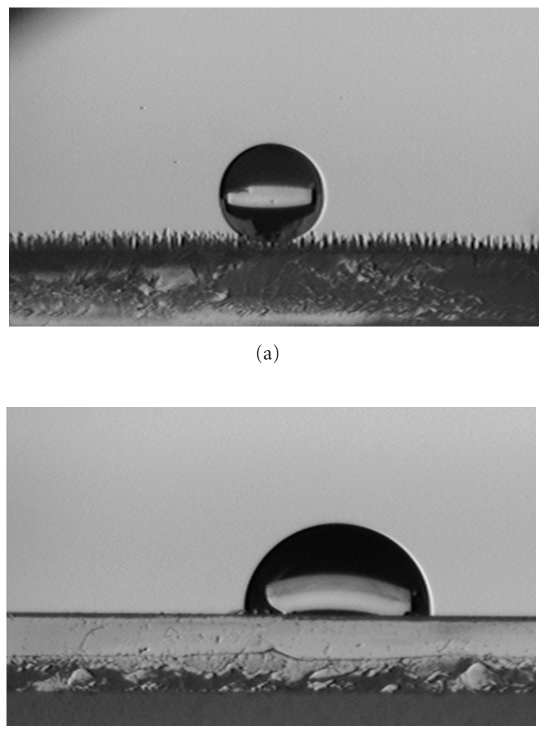
It is well known that the hydrophobicity of a surface is related with the surface structures [3, 12]. There are three theoretical models for the study of surface wettability.



(a)

(b)

Figure 2: SEM images of *Navodon septentrionalis* fish surface (a) and PDMS replica (b).



(a)

(b)

Figure 3: Comparison of static contact angle of PDMS positive replica (a) and PDMS flat sheet (b) without any additional chemical modification.

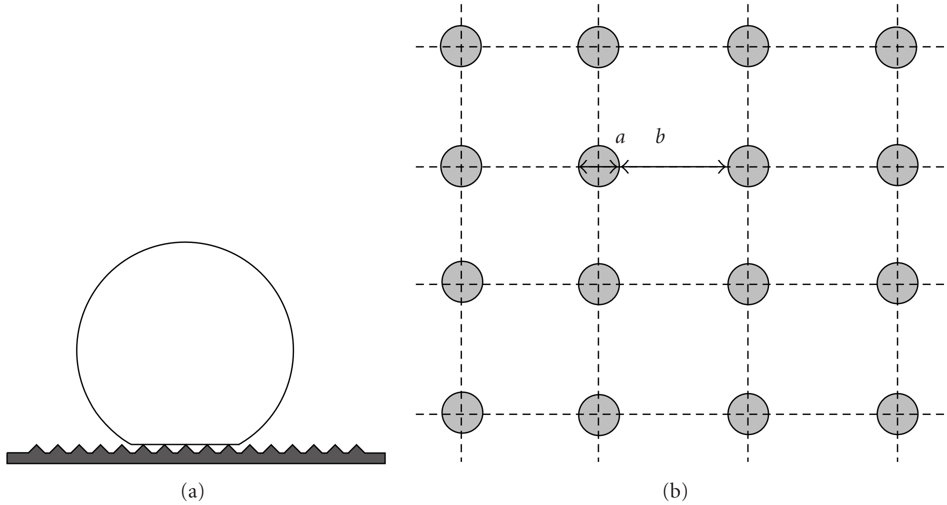


Figure 4: Circle-square graphics to calculate the contact angle of the replica surface.

Wenzel model describes the situation that liquid could wet the textured surfaces completely. C-B model is used for the study of liquid that does not wet the textured surfaces completely, and the third model is a combination of Wenzel and C-B models.

The superhydrophobicity of the replica in this paper was studied with the model of C-B:

$$\cos\theta_r = f_1 \cos\theta_1 + f_2 \cos\theta_2, \tag{1}$$

where f_1 is the fractional area of wetted solid surface, f_2 is the fractional area between the asperities ($f_1 + f_2 = 1$), and θ_1 and θ_2 are the two species each characterized by its own intrinsic contact angle. In this experiment, the intrinsic contact angle of air is $\theta_2 = 180^\circ$. Therefore, C-B equation can be simplified as

$$\cos\theta_r = f_1(\cos\theta_1 + 1) - 1, \tag{2}$$

where θ_r is C-B contact angle (apparent contact angle). To calculate the theoretic contact angle of the replicas surface with C-B model, a circle-square graphic was used (Figure 4). In the graphics, (a) and (b) are the diameter of solid awls and the spacing length of air on replicas, respectively. Therefore f_1 can be expressed as

$$f_1 = \frac{\pi(a/2)^2}{(a+b)^2}. \tag{3}$$

When using $a = 10\,\mu$m and $b = 100\,\mu$m, f_1 was calculated as 0.00649. Because the intrinsic contact angle θ_1 was measured as 100° (Figure 3(b)), the contact angle θ_r of the replica was calculated as 174.1° by using (2), which agreed with the measuring result.

4. Conclusion

A piece of fresh *Navodon septentrionalis* skin was replicated using PVA and PDMS elastomer by a two-step template method. The surface structure of *Navodon septentrionalis* fish skin was duplicated with high fidelity. Static contact angle of the replica was 173°, which agreed with the theoretic analysis based on Cassie-Baxter (C-B) model.

Acknowledgments

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