The preparation of Nepenthes Bio-inspired superhydrophobic surface primary microstructure

Jieqiong Lin, Mingwei Ma, Xian Jing
Changchun University of Technology, Changchun, Jilin, China

*Corresponding author e-mail: 497714025@qq.com

Abstract. 4Wetting phenomenon is an important phenomenon in nature, and it is related to our daily life closely. Therefore, it is of great practical significance to study wettability surface. Recently, based on the observation and measurement of Nepenthes surface, we realized the liquid or insects will roll down from the surface almost without resistance resulted from the lunate-shaped microstructure and its composite microstructure, which can make the surface possess superhydrophobic properties. Nepenthes Bio-inspired superhydrophobic primary microstructure was fabricated by the two-photon polymerization using femtosecond laser and characterized by developer and Zygo. The lunate are still intact after washing, so the character of hydrophobicity can be maintained. We demonstrate that our approach provide a novel way to fabricate such primary microstructures on the glass using femtosecond laser two-photon polymerization for practical applications in related area. 97714025@qq.com

1. Introduction
Wetting phenomenon is the theoretical basis for the study of the application of functional surfaces in many modern industries, and the size of contact angle is always become a criteria in the character of wettability. The contact angle of Superhydrophobic surface is greater than 90 degrees and the contact angle hysteresis is less than 5 degrees. Because of its unique self-cleaning effect and significant resistance reduction, superhydrophobic surfaces are widely used in national defense, daily life and many industrial fields. For example, it can be used for building glass, car windshields, sunglasses, submarine walls, etc.

After millions of years of evolution, there are many creatures in the biological world with superhydrophobic surfaces, such as lotus leaves [1], butterfly wings [2], rice leaves [3], and so on. Therefore, the research directions are mostly focused on combining bionics with surface chemistry to develop superhydrophobic surface.

But the wettability of the surface is mostly in the laboratory stage, mainly due to its poor mechanical stability, easy to damage, higher compression factor of product prices or others, which limits its scope of application to some extent under current circumstance.

We use the method of femtosecond laser two-photon polymerization. First, 3D plane was designed by CAD software. Then, the surface microstructure machining on Ormocer hybrid polymers was prepared by using 3D micro Taiwan. Finally, to ensure the stability of the surface of a lunate-shaped structure, the surfaces were observed with Zygo in the use of developer. It will be of important
theoretical and practical value to further study the microstructure of superhydrophobic surface and put it into practical application.

2. Establishment of a lunate microstructure model

Nepenthes[4-6] is a kind of special tropical plants which can be able to capture insects, it has a unique organ-pitcher, it contains 4 zones, called lid and peristome, slippery zone, transitional zone, digestive zone, respectively. The nectarglands of the peristome lure prey to the upper rim of the pitcher. The pitcher is smooth enough for insects to fall down into the bottom, then drowned by digestive juices secreted by the digestive zone. And these nepenthes use the insect prey as an additional source of indispensable nutrients to maintain its own element of nitrogen.

After the study of Nepenthes in recent years, a large number of experts and scholars suggested that there are great amount of crescent-shaped microstructure in the slippery zone surface inside the pitchers and covered with wax. Besides, the surface has the characteristics of superhydrophobic and extremely smooth.

Observation by Zygo, it reveals that numerous lunate-shaped microstructures are present downwards the Nepentch slippery zone, and it is distributed on the surface irregularly, as shown in Figure 1. Two-dimensional modeling of the microstructure which is presented in Figure 2 is done using the AutoCAD software.

![Fig 1 Slippery zone of the Nepenthes surfaces](image1)

![Fig 2 Microstructure measurement of two-dimensional lunate cells (Scale 100:1)](image2)
Because the main task of this paper is to measure the stability of the surface microstructure of Nepenthes primary lunate-shaped microstructure. It must have some differences between the superhydrophobic surface of plant surface and the practical surface using femtosecond laser two-photon polymerization processing. So we should make some necessary assumptions which are in conformity with the actual conditions: (1) To ensure the other conditions remain unchanged, only processing the primary roughness, lunate-shaped microstructure, in the photoresist surface, the surface still have hydrophobic properties. (2) To ignore the micro error of concave convex change caused in the machining process. In the other word, it is necessary to ignore the tiny air residual in the micro convex structure.

3. Materials and experimental setting

3.1 Materials.
OrmoCer is a UV-patternable inorganic-organic hybrid polymer for micro optical applications as micro lenses or diffractive optical elements. Detailed physical parameters of the processed hybrid polymers can be found in the Table 1.

After processing the OrmoCer hybrid polymer shows:
   a. excellent transparency in the near UV and visible wavelength range
   b. excellent mechanical properties
   c. high chemical and physical stability

| Table 1 Physical Parameters for Processed Ormocer Hybrid Polymer |
|---------------------------------------------------------------|
| Cured Ormocer hybrid polymer                                   |
| Volume shrinkage during UV curing                             |
| during hardbake                                               |
| [%]                                                          |
| [%]                                                          |
| CTE(20-100°C)                                                 |
| [ppm/K]                                                       |
| Water absorption                                             |
| [%]                                                          |
| Modulus of elasticity                                         |
| [GPa]                                                        |
| Hardness(by indentation)                                       |
| [MPa]                                                        |

3.2 Experimental setting
The laser beam emitted by a mode-locked Ti,Mai Tai DeepSee(80MHz repetition frequency, 100fs pulse width, 800nm wavelength), and its power is waken by an optical attenuator. Then it is expanded by a laser beam expander and focused on the hybrid polymer by objective (NA1.30, 100×, oil immersed). The process is controlled by a shutter. One portion of light is refracted by an objective lens and directed perpendicularly to the photoresist on the slide, the other portion of the light passes through the objective shoot at CCD. At the end of the experiment, the raw photoresist was washed off using the developer, and the microstructure was observed by Zygo and scanning electron microscopy.

4. Result and discussion
In order to verify the surface primary roughness of Nepenthes, lunate microstructure, has good stability, we fabricate microstructures in photoresist (Ormocer) surface using femtosecond laser two-photon polymerization method. As shown in Figure 3(a), we regarded the Nepenthes observed under Zygo as a template, then Biomimetic machining was performed. After the preparation observed by Zygo, the microstructure of the photoresist surface remains intact after the developer is washed off, as is presented in Figure 3(b).Then we selected one of the machining surface microstructure, in the other word, an individual lunate cells randomly (Fig 4). It is found that the height of the microstructure of a lunate cells is nearly 8μm, and the upper surfaces smooth, and when \( v = 100 \mu m/s \) , \( P = 20 mw \), the width of its across-sectional area 4μm (Fig 5). The experimental results show that the microstructure produced by femtosecond laser has a favorable character of stability, and it is difficult to be destroyed thoroughly,
and it also has higher machining accuracy simultaneously. Besides, it will exert a far-reaching influence on the development of the glass that we can fabricate such primary microstructures on it using femtosecond laser two-photon polymerization.

![Fig 3](image)

**Fig 3** Microstructure experiment preparation. (a) The lunate-shaped microstructure fabricated using femtosecond laser two-photon polymerization (b) The lunate-shaped microstructure observed by Zygo

![Fig 4](image)

**Fig 4** Diagram of a single microstructure

![Fig 5](image)

**Fig 5** Diagram of the size of upper surface of single microstructure
5. Conclusion
In recent years, although a large number of domestic scholars or some international scholars use different methods (sol-gel method, template method, self-assembly method) to prepare the superhydrophobic surface, but the stability of the surface microstructure are not very satisfactory. It is well known that the property of superhydrophobic surfaces resulted from their surface roughness. If the surface microstructure is destroyed, the roughness will be reduced, and the hydrophobic properties of the surface will be greatly poor or even disappeared. This is the biggest obstacle to put the superhydrophobic surfaces into practice so far.

In Conclusion, a large number of surface primary roughness microstructures, lunate microstructures, have been fabricated on the glass by femtosecond laser two-photon polymerization. We found that the surface micro structure remained intact after washing and other work, furthermore, the variation size of the upper surface after washing is only 1μm, this will be for the bionic surface put into practical application for Nepenthes an important reference.

Acknowledgments
This work was financially supported by National Natural Science Foundation of China (51375060) fund.

References
[1] Barthlott W, Neinhuis C. 1997. Purity of the sacred lotus or escape from contamination in biological surfaces. Planta 202: 1–8.
[2] Pan Hongbo, The Study on Preparation and Properties of Biomimetic Superhydrophobic Coating[D]. Sun Yat-sen University, SYSU, 2015.
[3] Yao J, Wang J N, Yu Y H, et al. Biomimetic fabrication and characterization of an artificial rice leaf surface with anisotropic wetting[J]. Chin Sci Bull, 2012(15):1362-1366.
[4] Bauer U, Grafe T U, Federle W. Evidence for alternative trapping strategies in two forms of the pitcher plant, Nepenthes rafflesiana[J]. Journal of Experimental Botany, 2011, 62(10):3683-3692.
[5] BI Kedong, SONG Xiaochuang, WANG Yujuan, YANG Juekuan, CHEN Yunfei, Anti-adhesion Mechanisms of Nepenthes Waxy Slippery Zone Surface [J]. JOURNAL OF MECHANICAL ENGINEERING, 2015, 51(23): 103-109.
[6] Wang Lixin, Zhou Qiang, Liu Qihang, Dimensions of Surface Structures of Slippery Zone in Nepenthes Pitchers And Bionic Design of Locust Trapping Plate[J]. Transactions of the Chinese Society for Agricultural Machinery, 2011, 42(1):233-235.