

Super-antiwetting with High Adhesion Property of Pitcher Plant

Ji K, Tomchak V, Xu K and F. Jee*

Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA

Abstract

The unique pattern of pitcher plants inner surface and its super-antiwetting property with high adhesion is reported. The surface is replicated by using a two-step approach with PDMS as the replicating material. The replica showed similar surface morphology and surface properties.

Keywords: Pitcher plants; Super-antiwetting

Introduction

The wetting property of a surface depends on both the surface morphology and the chemical composition of materials on the surface. Most super-antiwetting surfaces are made of hydrophobic materials, although some hydrophilic materials can also form super-antiwetting surfaces [1,2]. These surfaces have textures on the scale of 100 nm to 10 micrometers. In nature, two types of super-antiwetting surfaces exist on biological creatures [3-5]: One with low adhesion and another with high adhesion. Lotus leaves and water striders' legs are examples of super-antiwetting surfaces with low adhesion [6,7]; rose petals and gecko's toes are examples of the other. On a super-antiwetting surface with low adhesion, also commonly called an ultrahydrophobic surface, water droplets bead up and freely roll off the surface at very small tilting angle [8-10]. On super-antiwetting surfaces with high adhesion, water droplets do not slide with a large tilted angle or are firmly pinned to the surface even when the surface is placed upside down [11-13].

In both cases, contact angle measurement of water droplets is commonly used to characterize surface wettability. Typically, a super-antiwetting (ultrahydrophobic) surface has a water contact angle greater than 150° [14].

Method

It is generally recognized that the adhesive force of super-antiwetting surface is related to the surface roughness and morphology [15-17]: rough surface morphology results in low adhesion and superhydrophobicity, while smoother surfaces are adhesively hydrophobic. In general, the one with low adhesion has nanometer scale projection [18,19] or rough porous textures [20,21] on the microstructures on the surface, lowering the surface tension. As one example, lotus leaves, which have an ultrahydrophobic surface with low adhesion, have a hierarchical textured surface with microislands coated with nanoparticles. Typically, in super-antiwetting surfaces with high adhesion, well-aligned nanoparticle size array or papillae are present. Several different mechanisms of the high adhesion have been proposed, but the cause of the high adhesion remains controversial [22-24].

Here, we report that the surface of pitcher plants have super-antiwetting properties with high adhesion due to its unique surface morphology. We also report the surface property of replicas of surfaces of a pitcher plant. Inspired by practical applications of the super-antiwetting properties of surfaces such as self-cleaning, antifouling, friction reduction [25,26], or gecko toes' sticky properties, artificial replica of these surfaces have been developed by using a variety of approaches [27,28]. These replicated surfaces have various surface morphologies and various chemical compositions [29,30]. Our replica of the inner surface of pitcher plants showed similar high adhesion character.

Results and Discussions

The pitcher plant we used in this experiment was the North American Pitcher plant that belongs to the genus *Sarracenia* (Figure 1 left). The inner epidermis of the top section of the pocket-like digestive gland of the pitcher plant (the blue square in Figure 1 left) was collected for microscopic images (Figure 1 right) and for the replication. The inner surface has a fish scale-like morphology, pointing downward into the pocket of the pitcher plant (Figure 1 right). The pitcher plant's purpose of these spikes might be to prevent the escape of the caught bugs in the pocket.

The contact angle measurements (taken by an OCA15 contact angle meter, Future Digital Scientific, Long Island) showed a contact angle of $145 \pm 5^\circ$, with the surface holding a water droplet tightly without dropping even when the plate is held upside down, suggesting the super-antiwetting property with high adhesion to the surface

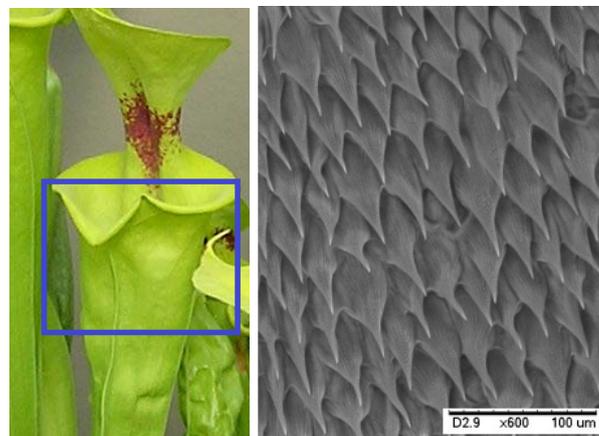


Figure 1: Left: Picture of a North American pitcher plant leaf. Right: SEM images of the inner epidermis of the top section of the pocket-like digestive gland of the pitcher plant.

*Corresponding author: Karen Xu, Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA, Tel: 12158952562; E-mail: hj56@drexel.edu

Received January 05, 2017; Accepted February 09, 2017; Published February 16, 2017

Citation: Ji K, Tomchak V, Xu K, Jee F (2017) Super-antiwetting with High Adhesion Property of Pitcher Plant. J Nanomed Nanotechnol 8: 424. doi: 10.4172/2157-7439.1000424

Copyright: © 2017 Ji K, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

(Figure 2). This contact angle was caused by the morphology of inner surface of the pitcher plant's pocket. Each scale's spike is approximately 30 micrometers in length. The tips of the spike are in the nanometer-scale.

Next, we demonstrated the capability to replicate the surface morphology by implementing a template method. Replication from a natural template might be the most effective and simple way to reproduce complex surface morphology in nature. While a variety of methods have been developed to mimic super-antiwetting surfaces of plant leaves, a facile approach is to create a template to replicate the surficial morphology [31]. One of the most popular materials for replicating surface structures is Polydimethylsiloxanes (PDMS) [32], which is an industrially important soft material that have been used for sealants, adhesives, damping fluids, cosmetics, et al. [33] Besides from its characteristically viscoelastic property, PDMS is also noted for being hydrophobic. PDMS has been used for surface geometry replication by casting a viscous PDMS liquid for solidification without any sophisticated treatment of the surface. A resolution of around 20 nm has previously been reached by using this approach [34], which validated the effectiveness of this method for replicating surface morphologies.

In this method, a mixture of liquid PDMS and its curing agent (ratio of 10:1, Figure 3a) is casted onto the inner surface of the pitcher plant in order to make a negative template of the structures of the textured surface. This mixture is a viscous and transparent liquid. When the

PDMS solidifies at room temperature for 24 hours, the PDMS layer is peeled off, resulting in a complementary topographic surface structure of the original template surface (negative template, Figure 3b and 3c). If off-peeling is difficult, soaking the leaf and the negative template in water for a couple of hours helps with removing the leaf without damaging the negative template. Although the curing time can be shortened to 30 min at 80°C, longer time at room temperature was adopted in our experiment to avoid any deformation of the surface of the inner epidermis of the pitcher plant. The negative template was then coated with a monolayer of nonstick trimethylchlorosilane (TMCS) by thermal evaporation in a vacuum, or simply by leaving both the negative template and TMCS solvent next to each other in a desiccator (Figure 3d, called silanization step). Then on PDMS nonstick template, another replication of PDMS is performed. At this step, a mixture of PDMS liquid and the curing agent at 5:1 was used because this mixture was less viscous so it could penetrate better into the holes of the negative template so the surface feature are better replicated than the mixture at the 10:1 ratio. After separation, the newly formed PDMS film is a replica of the textured surface pattern of the pitcher plant (positive replica, Figure 3e). The negative template can be reused to replicate the surface of the pitcher plant.

The fabrication process allows us to prepare an effective replica. PDMS was successfully used to transfer the surface morphology of the pitcher plant in a simple two-step approach. Figure 3e shows that the morphology on the pitcher plant was extremely close to full replication from the PDMS. The process can be used to mass replicate the morphologies of the pitcher surface. The tip morphology was observed on the positive replica as well, however, the tips of replica were connected to the surface, probably because the tips of spikes were forced onto the surface by the viscous PDMS when casting PDMS. Further improvement of the PDMS recipe and the process seems necessary to replicate the morphology more precisely. The contact angle of the positive replica is $140 \pm 8^\circ$, which is about the same as those on the pitcher plant surface (Figure 4). As comparison, the contact angle of a flat PDMS surface is about 105° . Furthermore, the water droplets pinned on the surface would not fall off, even when held upside down (Figure 4). The mimicked PDMS shows similar micro- and nanostructures to those on pitcher plant surface and the same super-antiwetting abilities with high adhesion behavior. The replication can be repeated and all the replica showed similar morphology and the water contact angle, indicating the fabrication process was highly reproducible and controllable.

Conclusions

In summary, this work demonstrated the unique pattern of pitcher plants and their super-antiwetting properties with high adhesion. The study introduced another super-antiwetting surface morphology with high adhesion that may help with understanding this phenomenon.

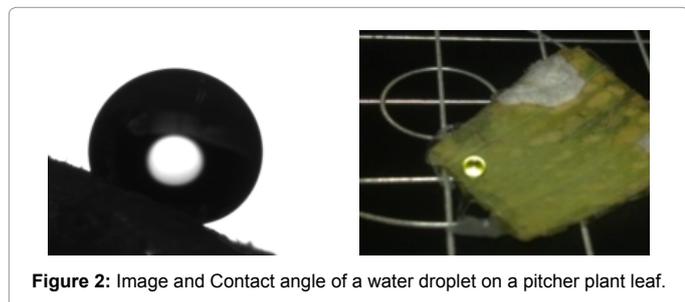


Figure 2: Image and Contact angle of a water droplet on a pitcher plant leaf.

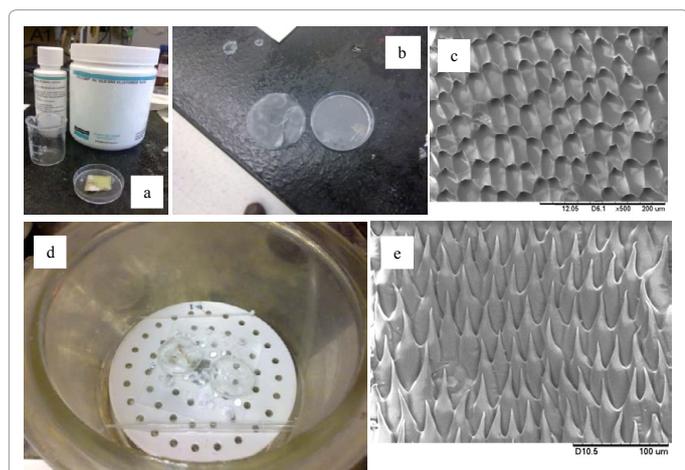


Figure 3: a) PDMS used in this experiments was obtained from Galco Industrial Electronics Inc. (Sylgard-184 silicone elastomer kit). b) A picture of the a negative template prepared from the solidification of PDMS on the pitcher's plant surface. c) SEM image of the negative template. d) Both the negative template and TMCS solvent were left next to each other in a desiccator in order to evaporate a nonstick monolayer of TMCS onto the negative template. e) SEM image of a replicated PDMS sample of the pitcher plant.

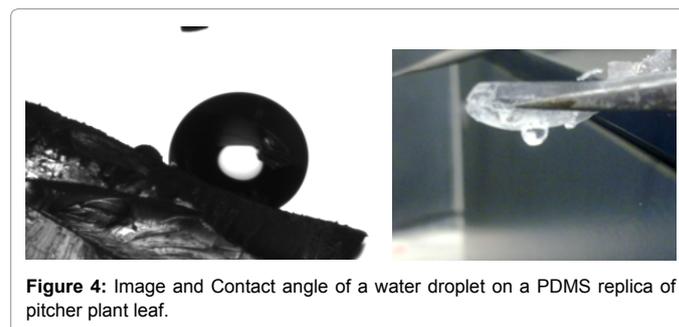


Figure 4: Image and Contact angle of a water droplet on a PDMS replica of pitcher plant leaf.

We also demonstrate the formation of a replication of the surface by using a two-step approach by using PDMS as the template material. The method is effective to transfer the surface morphology of the pitcher plant onto a PDMS surface. We are also interested in whether this replica can be used for bug catching just as the pitcher plant does, and further work will be reported in the future.

Acknowledgement

The authors thank the Longwood Garden for the pitcher plant samples.

References

- Zhu Y, Gao C, He T, Liu X, Shen J (2003) Layer-by-layer assembly to modify poly(L-lactic acid) surface toward improving its cytocompatibility to human endothelial cells. *Biomacromol* 4: 446-452.
- Feng L, Song Y, Zhai J, Liu B, Xu J, et al. (2003) Creation of a Superhydrophobic Surface from an Amphiphilic Polymer. *Angew Chem Int Ed* 42: 800-802.
- Adamson AW (1990) *Phys Chem Surf*. Academic Press, New-York NY.
- Barthlott W, Neinhuis C (1997) Purity of the sacred lotus, or escape from contamination in biological surface. *Planta* 202: 1-8.
- Teisala H, Tuominen M, Kuusipalo J (2011) Adhesion Mechanism of Water Droplets on Hierarchically Rough Superhydrophobic Rose Petal Surface. *J Nanomater*.
- Liu KS, Zhang ML, Zhai J, Wang J, Jiang L (2008) Bioinspired construction of Mg-Li alloys surfaces with stable superhydrophobicity and improved corrosion resistance. *Appl Phys Lett* 92: 183103.
- Gao XF, Jiang J (2004) Biophysics: water-repellent legs of water striders. *Nature* 432: 36.
- Lau KKS, Bico J, Teo KBK, Chhowalla M, Amaratunga GAJ, et al. (2003) Superhydrophobic Carbon Nanotube Forests. *Nano Lett* 3: 1701-1705.
- Quere D (2002) Surface chemistry: Fakir droplets. *Nature Mater* 1: 14-15.
- Yoshimitsu Z, Nakajima A, Watanabe T, Hashimoto K (2002) Effects of Surface Structure on the Hydrophobicity and Sliding Behavior of Water Droplets. *Langmuir* 18: 5818-5822.
- Autumn K, Liang YA, Hsieh ST, Zesch W, Chan WP, et al. (2000) Adhesive force of a single gecko foot-hair. *Nature* 405: 681-685.
- Bhushan B, Her EK (2010) Fabrication of superhydrophobic surfaces with high and low adhesion inspired from rose petal. *Langmuir* 26: 8207-8217.
- Feng L, Zhang Y, Xi J, Zhu Y, Wang N, et al. (2008) Petal effect: a superhydrophobic state with high adhesive force. *Langmuir* 24: 4114-4119.
- Liu K, Yao X, Jiang L (2010) Recent developments in bio-inspired special wettability. *Chem Soc Rev* 39: 3240-3255.
- Yang X, Liu X, Lu Y, Zhou S, Gao M, et al. (2016) Controlling the Adhesion of Superhydrophobic Surfaces Using Electrolytes Jet Machining Techniques. *Sci Reports* 6: 23985.
- Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, et al. (1997) Light-Induced Amphiphilic Surfaces. *Nature* 388: 431-432.
- Nosonovsky M, Bhushan B (2009) Superhydrophobic surfaces and emerging applications: non-adhesion, energy, green engineering. *Curr Opin Colloid Interface Sci* 14: 270-280.
- Erbil HY, Demirel AL, Avci Y, Mert O (2003) Transformation of a simple plastic into a superhydrophobic surface. *Science* 299: 1377-80.
- Wang XB, Liu YQ, Zhu DB (2002) Two- and Three-Dimensional Alignment and Patterning of Carbon Nanotubes. *Adv Mater* 14: 165-167.
- Uhlmann P, Ionov L, Houbenov N, Nitschke M, Grundke K, et al. (2006) Surface functionalization by smart coatings: stimuli-responsive binary polymer brushes. *Prog Org Coat* 55: 168-174.
- Mock U, Foerster R, Menz W, Ruehe J (2005) Towards ultrahydrophobic surfaces: biomimetic approach. *J Phys Cond Matter* 17: S639-S648.
- Boscher ND, Carmalt CJ, Parkin IP (2006) Atmospheric pressure chemical vapor deposition of WSe₂ thin films on glass-highly hydrophobic sticky surfaces. *J Mater Chem* 16: 122-127.
- Zhao WJ, Wang LP, Xue QJ (2010) Fabrication of low and high adhesion hydrophobic Au. *J Phys Chem C* 114: 11509-11514.
- Lai YK, Gao XF, Zhuang HF, Huang JY, Lin CJ, et al. (2009) Designing Superhydrophobic Porous Nanostructures with Tunable Water Adhesion. *Adv Mater* 21: 3799-3803.
- Burmeister F, Kohn C, Kuebler R, Kleer G, Bläsi B, et al. (2005) Applications for TiAlN- and TiO₂-coatings with nanoscale surface topographies. *Surf Coat Tech* 200: 1555-1559.
- Wang J, Hu J, Wen Y, Song Y, Jiang L (2006) Hydrogen-Bonding-Driven Wettability Change of Colloidal Crystal Films: From Superhydrophobicity to Superhydrophilicity. *Chem Mater* 18: 4984-4986.
- Wang S, Feng L, Jiang J (2006) One-Step Solution-Immersion Process for the Fabrication of Stable Bionic Superhydrophobic Surfaces. *Adv Mater* 18: 767-770.
- Zhang J, Huang W, Han Y (2006) Wettability of zinc oxide surfaces with controllable structures. *Langmuir* 22: 2946-2950.
- Wang DA, Wang XL, Liu XJ, Zhou F (2010) Engineering a titanium surface with controllable oleophobicity and switchable oil adhesion. *J Phys Chem C* 14: 9938-9944.
- Bhushan B, Jung YC, Niemietz A, Koch K (2009) Lotus-Like Biomimetic Hierarchical Structures Developed by the Self-Assembly of Tubular Plant Waxes. *Langmuir* 25: 1659-1666.
- Nicolas M, Guittard F, Geribaldi S (2006) Stable Superhydrophobic and Lipophobic Conjugated Polymers Films. *Langmuir* 22: 3081-3088.
- Samuel JD, Jeyaprakash S, Ruehe J (2004) A Facile Photochemical Surface Modification Technique for the Generation of Microstructured Fluorinated Surfaces. *Langmuir* 20: 10080-10085.
- Whitesides GM, Ostuni E, Takayama S, Jiang X, Ingber DE (2001) Soft lithography in biology and biochemistry. *Annu Rev Biomed Eng* 3: 335-73.
- Zhao XM, Xia YN, Whitesides GM (1997) Soft lithographic methods for nanofabrication. *J Mater Chem* 7: 1069-1074.