Super-antiwetting with High Adhesion Property of Pitcher Plant

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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, lotus leaves have 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 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 ± 5°, 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.

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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.

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 ± 8°, 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.
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 reported it in the future.

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References