HIGH ENERGY SURFACE AS A RECEPTOR IN ELECTROSPINNING
A Good Switch for Hydrophobicity to Hydrophilicity

by

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The lotus leaf surface is modified by covering nanofibers to check its wetting property. The well-known lotus effect of the modified surface is greatly weakened, and a hydrophilic property is found. The geometric potential theory is used to explain the phenomenon, it shows that the two adjacent nanofibers can produce a high geometric potential to push water molecules to move along the fibers, as a result, a hydrophilic surface is predicted after surface modification. An experiment is designed to elucidate the main factors affecting the wetting property of the modified surface of lotus leaf.

Key words: *high energy surface, electrospinning, surface modification, nanofibers, geometric potential theory, lotus effect*

Introduction

The lotus possesses a peculiar water-repellent characteristic that enhances the mobility of droplets for self-cleaning purpose [1, 2]. The super-hydrophobic property of lotus leaf has been extensively studied. Lotus leaf has a high surface energy (geometric potential), resulting from multi-scale micro/nanostructures, and several design ideas have been inspired by lotus leaf [3, 4]. In recent years, smart surface with wettability transition property has become a research hotspot for many potential application [5-10]. The surface wettability can be modified by the chemical manner [11], coating [12], lasers [13], ultraviolet-driven method [14], and so on.

Ren *et al.* [15] prepared an oil/water separation material with TiO_2 at SA/CS coating, which could be converted from superhydrophobicity to superhydrophilicity under ammonia treatment, and the superhydrophobicity could be restored again after heating treatment. Xia *et al.* [16] and coworkers prepared SIPN hydrogels which showed rapid conversion from being hydrophilic at 20 °C to being hydrophobic at 45 °C. Ding *et al.* [17] reported a strategy to transform the membrane's hydrophobicity into high hydrophilicity through a one-step levodopa (l-DOPA)/3-amino-propyltriethoxysilane (APTES) reaction. Guo *et al.* [18] prepared a counterion-switched reversibly hydrophilic and hydrophobic surface of TiO_2-loaded polyelectrolyte membrane by layer-by-layer assembly of PSS and PDDA containing TiO_2 at

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PDDA nanoparticles on the hydrolyzed PAN substrate membrane. The obtained membranes showed different hydrophilicity and hydrophobicity with various counterions.

This paper shows a surface's wetting property depends upon its geometric potential. The change of the surface geometric potential can convert the hydrophobicity to hydrophilicity, and vice versa.

Geometric potential and lotus effect

Many leaves of aquatic plants, notably the lotus leaf, have gained much attention because of their super-hydrophobicity, self-cleaning characteristics, and outstanding mechanical properties. The super-hydrophobicity of lotus is primarily due to multi-scale micro/nanostructures on the surface [19-21]. The secret of water repellency and self-cleaning properties of lotus have been found out to be induced by an intrinsic hierarchy built by randomly oriented small hydrophobic wax tubules on the top of convex papillae of epidermal cells [22]. Figure 1 shows digital images of lotus leaf. The veins on the lotus leaf exhibit fractal characteristics with self-similarity.

By using the SEM observation, the representative images of the lotus surface are demonstrated in fig. 2. The upper epidermis of lotus leaf is characterized by micro/nanosize protrusions epidermal cells and valleys uniformly, which are decorated with an additional layer of wax crystalloids. The lower epidermis of lotus leaf is composed of tree bark-like cuticular folds which distribute all over the whole surface. The micro structure of vein is shown in fig. 3. It is noted that the protrusions lay on both side of the upper epidermis along with vein.

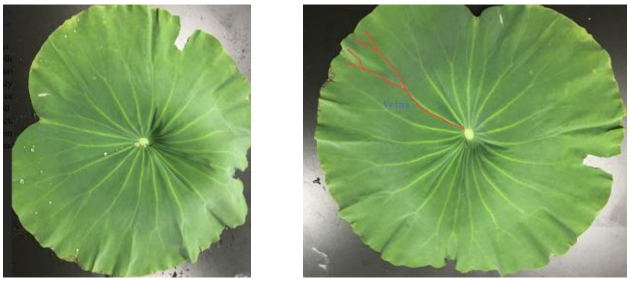

Figure 1. Lotus leaf

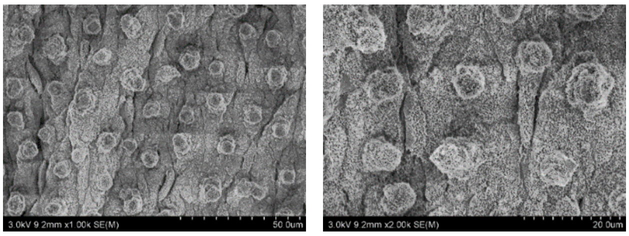

Figure 2. The SEM images of the top surfaces of lotus between the veins

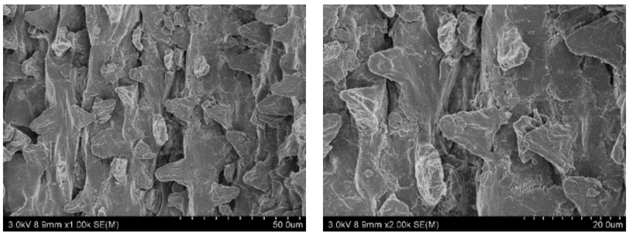

Figure 3. The SEM images of the top surfaces of lotus vein

The geometric potential theory [23-26] implies that any surface can produce a force, it can be gravity, Casimir force, capillary force or others. The geometric potential theory can well explain how to form a shaped fiber or an unsmooth fiber in the spinning process [27, 28], the smart adhesion by the surface treatment [29], the cell orientation during the cell culture [30], and capillary effect [31, 32]. It is also interesting to find that Fangzhu, an ancient device in more than 5000 years ago, collect water from air, works according to the geometric potential of the Fangzhu's surface [33].

The geometric potential produced by a surface can be expressed [33-35]:

$$E = \frac{k}{r} \tag{1}$$

where E is the geometric potential, r – the equivalent radius of the surface, and k – a constant. The boundary-induced force can be obtained:

$$F = -\frac{\partial E}{\partial r} = \frac{k}{r^2} \tag{2}$$

When the surface radius becomes smaller, a higher force is produced. When the surface of the water molecule approaches to nanoscale protrusions on the surface, the geometric potential can produce a high attraction force which attracts water molecules onto their surface. Figure 4 illustrates the mechanism of a drop of water formation. Along with more and more water molecules are attached on the lotus protrusions, water molecules can form a water bridge between two micro size protrusions. For the distance is very small, two water bridges will attract and get together into a big droplet of water, see fig. 4.

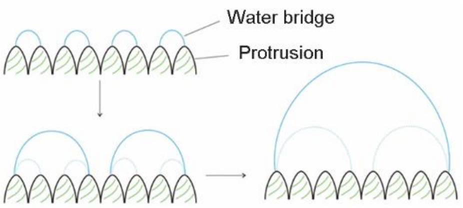

Figure 4. The mechanism of droplet formation on lotus surface

Lotus leaf’s surface treatment by electrospinning

Electrospinning has attracted considerable attention due to its cost-effectiveness and versatility [36-41]. As one of the most efficient techniques, it is being used to fabricate nanofibers ranging from single fiber to ordered arrangement fibers. Electrospinning is not only employed in university laboratories, but is also increasingly being applied in industry.

The morphologies and microstructures of top surface of lotus leaf covered with electrospun polyvinyl alcohol (PVA) nanofibers were determined using a SEM, Hitachi S-4800, Tokyo, Japan, see fig. 5. The PVA nanofibers exhibited uniform morphologies and randomly distributed that adhered to each other.

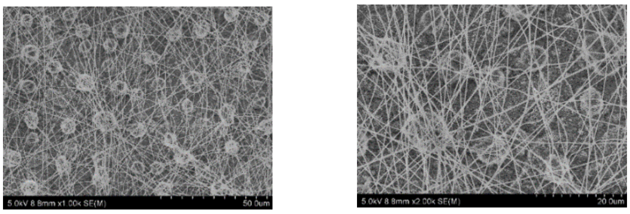

Figure 5. The SEM images of modified surface of a lotus leaf with PVA nanofibers

When a water drop is placed on the two adjacent nanofibers, it will move along the fibers [42] due to a capillary-like force which is induced by the boundaries of nanofibers, and it will spread to other adjacent fibers, and a liquid column is formed [43-46]. The boundary-induced force will produce an unsmooth boundary of the water drop as illustrated in fig. 6. The geometric potential becomes weak when the distance between two adjacent fibers becomes wide. For an aligned nanofiber membrane, a capillary-like force is produced, which is parallel to the fiber orientation, while for a randomly distributed nanofiber membrane, the boundary-induced force induced by adjacent nanofibers are randomly directed.

When the PVA nanofibers were spun onto the surface of the lotus leaf, they randomly distributed. Droplets on the disordered nanofibers may spread outwards, see fig. 7. Hence, the wettability of the lotus leaf can be controlled by nanofiber, from a hydrophobicity to hydrophilicity.

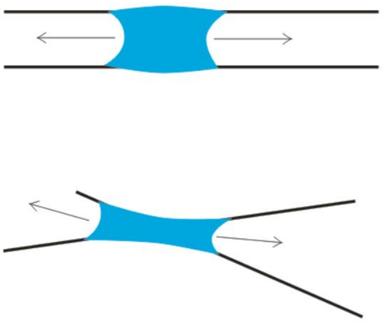

Figure 6. The boundary-induced force between two adjacent nanofibers

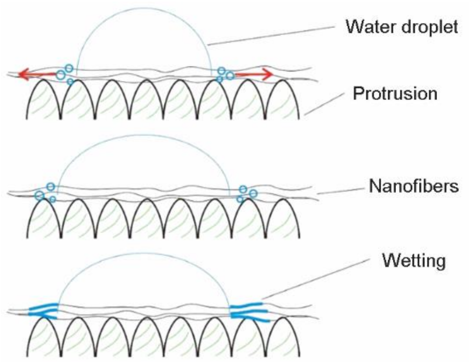

Figure 7. The mechanism of droplet wetting in nanofibers on lotus surface

Experiment verification

The PVA used in this experiment was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), and directly used as received without any further purification. It was stored at room temperature and alcoholysis degree of the PVA was 98-99.0 mol%. For this study, lotus leaves were obtained from a lotus pool in Suzhou.

The PVA solution was prepared at room temperature by dissolving the polymer in deionized water with a concentration of 8 wt.%. The PVA solution was magnetically stirred at 80 °C for two hours to ensure complete dissolution and prepared for a uniform and transparent solution.

The equipment for electrospinning was composed of a high voltage power supply, syringe pump, and receptor. The receptor consisted of lotus leaf and metal plate. The lotus leaf was placed on the metal plate, as shown in fig. 8. The solution was loaded into a 10 mL syringe. The needle had an inner diameter of 0.7 mm. The syringe pump was used to dispense the polymer solution at a feed rate of 1 mL per hour. The needle-to-receptor distance was maintained at 15 cm. The polymer solution was spun at room temperature at a driving voltage of 20 kV. The needle was positively charged and receptor was negatively charged. Continuous nanofibers were deposited on the surface of the lotus leaf and collected in the form of non-woven nanofiber membrane.

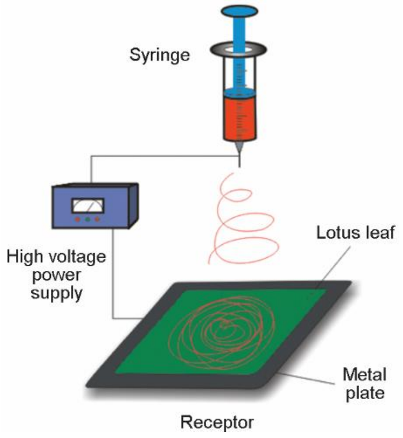

Figure 8. The equipment for electrospinning with lotus leaf as a receptor

Results and discussion

The nanofibers were deposited on the lotus leaf's surface due to the electric field force. The thickness of the formed nanofiber membrane was characterized by the spinning time with 5, 10, 30 seconds, 1 minute, 5 minutes, and 10 minutes, respectively. For comparison, nanofibers were also deposited on a foil receptor for 10 minutes, see tab. 1. Sample 1 was a lotus leaf, Samples 2-7 were membranes deposited on the lotus leaf with different spinning time, and Sample 8 was membrane deposited on the foil. With the electrospinning time increasing, the thickness and nanofibers quantities increased, fig. 9.

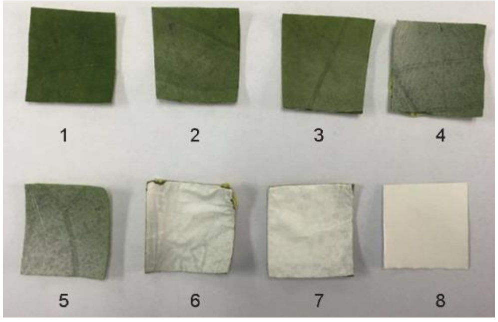

Figure 9. The images of the Samples;
1 – lotus leaf, (2-7) – nanofiber membrane on lotus with different spinning time, and 8 – nanofiber membrane on foil

Table 1. Electrospinning time for different samples

Sample no.	1	2	3	4	5	6	7	8
Receptor	Lotus	Lotus	Lotus	Lotus	Lotus	Lotus	Lotus	Foil
Electrospinning time	0 s	5 s	10 s	30 s	1 min	5 min	10 min	10 min

Water drops were placed on the samples surface using a syringe with 0.7 mm inner diameter needle. The water drops on the different surface were shown in fig. 10. The fibers on the lotus leaf's surface played an important role in the wetting performance. Spherical water drop was floating on the top surface of the lotus leaf. While the water drops became ellipse spheres on the lotus leaf's surfaces covered with nanofibers. With the increasing of the nanofibers quantities, the water drops on the lotus leaf's surfaces gradually became more flat, and the surfaces became wetted. It demonstrated that the water drop spread on the nanofibers surface.

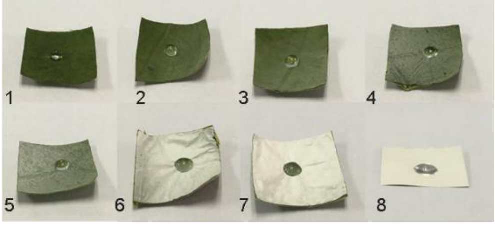

Figure 10. Images of water drops on different surfaces

Contact angle (CA) was analyzed using a Kruss DSA 100 apparatus (Kruss Company, Germany). The sample was placed on a moveable table. A motor was employed to drive a syringe to pump water steadily into a drop. Each sample measured three times and its mean value was used. Table 2 gave water contact angles of different surfaces. The contact angle on the top surface of lotus leaf in the ambient air was about 154.5°. With the increase of the nanofibers quantities, the contact angle decreased, shown in fig. 11. The sample presented hydrophilicity, when the nanofibers increased to a critical value on the lotus leaf's surface, which was finally switched hydrophobicity to hydrophilicity.

Table 2. Contact angles on different surfaces

Sample no	1	2	3	4	5	6	7	8
Contact angle [°]	154.5	99.5	92.3	81	71.1	65	58	49.3

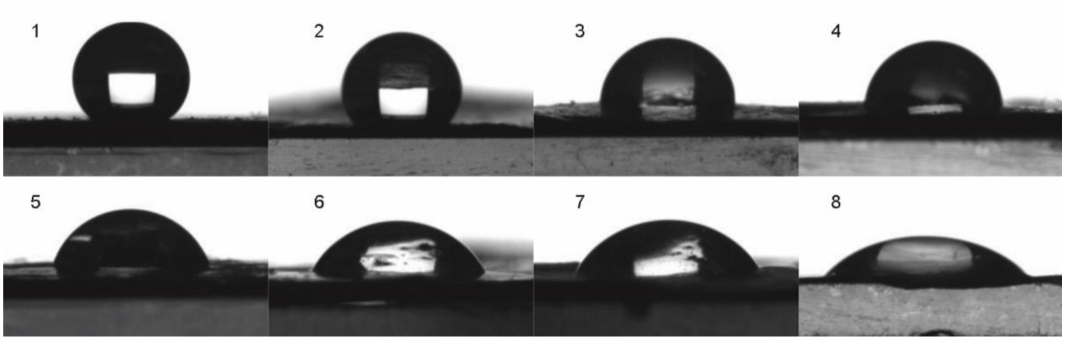

Figure 11. The images of contact angle on the surfaces of different samples

Conclusion

This paper revealed the mechanism of lotus effect and water droplet's spreading in nanofibers on the lotus leaf's surface, which could be well explained by the geometric potential theory. The lotus leaf was used as a receptor in the electrospinning process, and the wetting characteristics of modified surface was changed. Results showed that drop wetting length and contact angle increased with nanofibers increasing. The thickness of the nanofiber membrane played an important role in switching from hydrophobicity to hydrophilicity. This was an excellent method for understanding wetting on nanostructured surfaces. It demonstrated a simple method for surface wettability that can be manipulated reversibly in a controlled manner from a hydrophilic state to a hydrophobic state, and had a great potential in many surface applications.

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