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Analysis and Mimicking on Superhydrophobic Structure of Several Plant Leaves

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Abstract

Contact angle of several plant leaves such as lotus, canna, reed and bluegrass were 152.6 ° , 150.3 °, 151.4 °and 150.6 ° respectively, their microstructure were observed by scanning electron microscopy, It found that they are composite structure of micro and nanometer. According to this principle, experiment prepared template of polystyrene microspheres with diameter of 722nm, the copper atoms filled the voids of the template by electrochemical deposition, removed template, obtained copper surface with regular arrangement of spherical cave structure, then modified copper surface with fluorosilane, its contact angle surface is 156.3 °. Analyzed the factors associated with superhydrophobicity, the key parameters are diameter of the polystyrene microspheres and electrodeposition time.

Key words: *superhydrophobic, structure, template, deposition, plant leaves*

1. Introduction

Superhydrophobicity of solid surface is an important physical property, the contact angle was a parameter measured wettability of the solid surface [1]. The contact angle is greater than 150 °, when water droplets rests on the solid surface, this is called super-hydrophobic surface. Superhydrophobic surface has a wide range of applications such as self-cleaning, anti-corrosion, anti-snow, antioxidant, which has become one of the hot spot of scientists and engineers research [2-4].

In this paper, microstructures of lotus leaves, canna leaves, reed leaves and bluegrass leaves were observed by scanning electron microscope. Mimicked the plant leaves microstructure, experiment prepared regular arrangement of spherical cavities on copper surface by electrodeposition methods, then modified copper surface with fluorinesilane, obtained superhydrophobic copper surfaces.

2. Plant Leaves Experiment

2.1. Contact Angle Measurement

Some lotus leaves, canna leaves, reed leaves and bluegrass leaves are collected from the Children Park and the Nanhu Park, Changchun, Jilin Province, contact angle of four typical leaves were measured by contact angle meter (DSA100, accuracy of 0.1°, made by KRUSS). The volume of water droplets was 5μL in measuring experiment, Each values of contact angle was measured for 5 times, taking their average, which were 152.6°, 150.3°, 151.4° and 150.6 ° respectively, they are all superhydrophobic.

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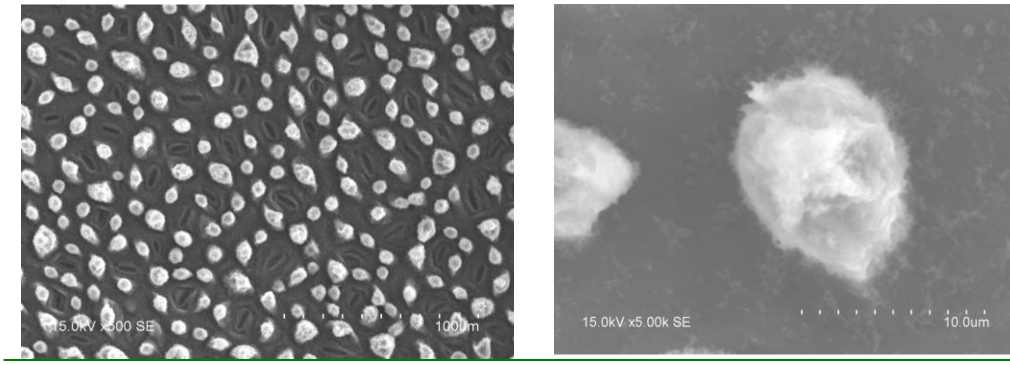
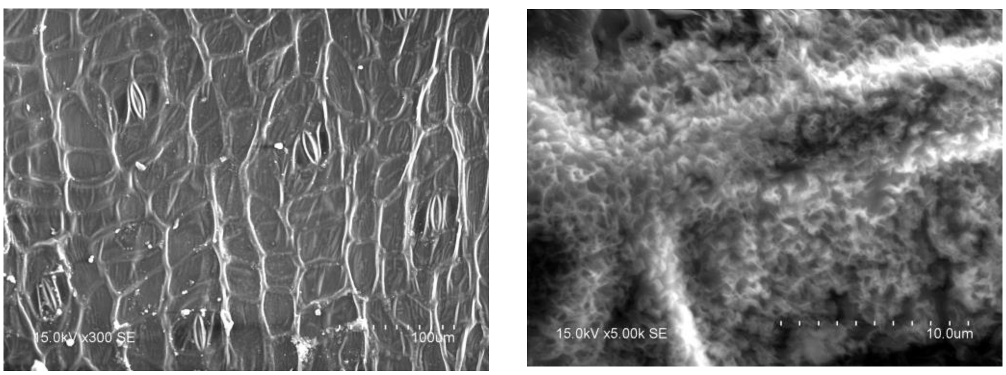
2.2 Scanning Electron Microscopy Observation

Lotus leaves, canna leaves , reed leaves and bluegrass leaves were fixed on the stage respectively, through processing of spraying gold, experimental samples were observed through scanning electron microscope, their microstructures are shown in Figure 1, Figure 2 , Figure 3 and Figure 4 respectively.



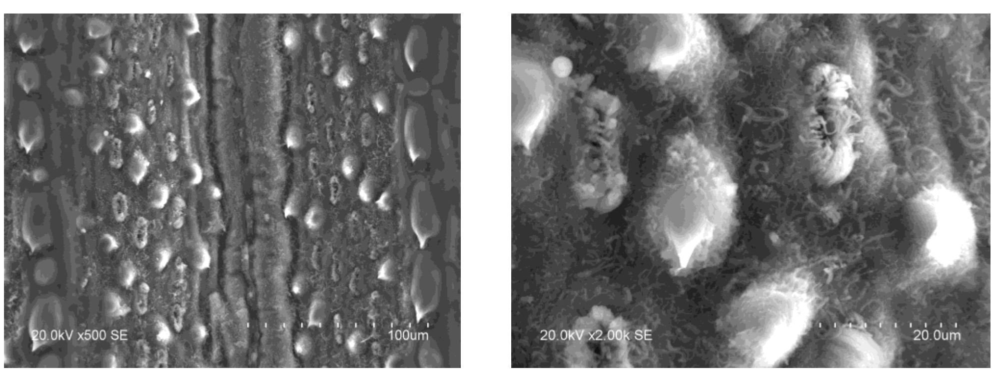
（a） （b）

Figure 1. Microstructure of Lotus Leaves



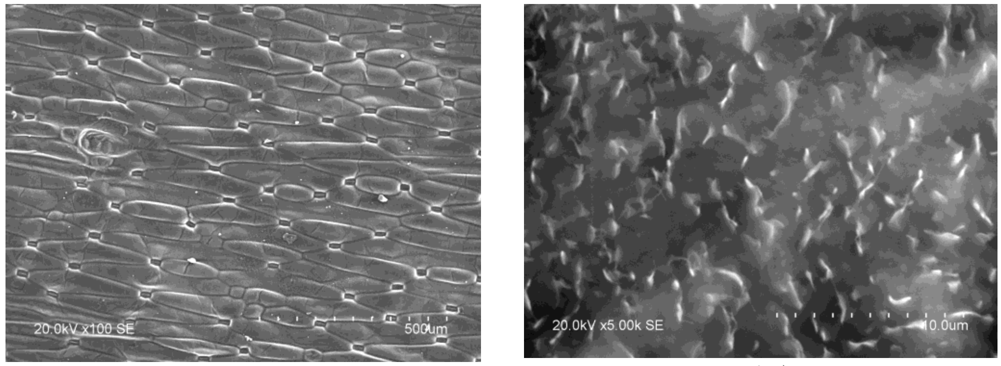
（a） （b）

Figure 2. Microstructure of Canna Leaves



（a） （b）

Figure 3. Microstructure of Reed Leaves



(a) (b)

Figure 4. Microstructure of Bluegrass Leaves

3. Superhydrophobic Mechanism Analysis

Generally considered that superhydrophobic of solids surface has two important factors [5-6], one factor is the chemical composition of the solid surface, another factor is microstructure of the solid surface, microstructure is a relatively important factor. This paper only from the perspective of the microstructure to interpret wettability of lotus leaves, canna leaves, reed leaves and bluegrass leaves.

Cassie and Baxter [7] think that water droplets on contact with a rough surface is a composite contact, the miniaturization scale of the surface structure is smaller than water droplets. Meanwhile, because of the surface tension of water droplets, according to Cassie model water droplets can not fill the grooves of the rough surface. Some air is trapped under the water droplets. Actual surface is composed of the solid and gas together, Cassie Cassie equation is

$$\cos\theta_c = f_s(1+\cos\theta)-1 \quad (1)$$

In Eq.1, θ_c represents the apparent contact angle of rough surface, f_s represents area ratio of which water droplets contact the solid substrate area divided by the composite interface area. θ represents a contact angle of flat surface same chemical compose as rough surface.

Lotus leaf surface distribute micron-scale mastoid with hemispherical structure, the mastoid diameter is about 5-9μm. There is a lot of nanometer scale fibrillar structure on the mastoid, its average diameter is about 90-120 nm shown in Figure 1. The micro-nanostructures can form a layer of film in the lotus leaves surface by capturing effectively air, In addition, the lotus leaf surface is covered with a layer of wax which can reduce the free energy of leaves surface, the 2 factors have great contribution for the lotus leaves superhydrophobicity. Lotus leaves surface with special micro-nanometer composite structure can effectively reduce the degree of contact between the solid and the liquid , this can affect length and the shape of the three-phase contact line, which can greatly reduce the roll angle , Making water drops rolling easily from lotus leaves, it exhibit good superhydrophobic and self-cleaning function.

Canna leaves also showed super-hydrophobic feature and self-cleaning function, which image of scan electron microscope are shown in Figure 2. Canna leaves surface distributed regular some grid with approximate rectangle, further amplification electron microscope image of canna leaves, as can be seen, micron-level grids arranged regularly some folds with nano-scale, these folds size are about 300-500 nm. Canna leaves surface formed binary complex structure, which conducive to capture air, forming an air film on the leaves surface, so that it has the super-hydrophobic surface properties by Cassie theory.

Reed leaves surface is micro-nano composite structure which similar to lotus leaf, but the mastoid of the reeds leaf arranged orderly direction along the leaves edges, arranged disordered in the vertical direction of leaf edges, its electron microscope image are shown in Figure 3.

Bluegrass leaves surface covered convex hull with peanut-shaped, the average length of the convex hull is about 100-200μm, average width of the convex hull is about 40-60μm. further amplification electron microscope image of bluegrass leaves, as can be seen, some nanoscale petals arranged regularly on the convex hull, its electron microscope image are shown in Figure 4. This micro-nano composite structure can effectively absorb air, this structure is important factor of superhydrophobicity.

4. Mimicking Plant Leaves Structure

4.1. Electrodeposition Experiment

First, polystyrene microspheres powders were made from polymerization of styrene (Tianjin Guangfu Fine Chemical Research Institute) and sodium dodecyl sulfate (Shanghai Reagent Factory).Secondly, ethanol and water (volume ratio 1:1) as a dispersion medium, which is mixed with polystyrene microspheres (mass fraction of 1%). Latex colloidal of polystyrene can be prepared. Finally, the colloidal of polystyrene microspheres have assembled on the gas-liquid interface, which can obtain the template.

Electrochemical deposition is used widely in preparation of the template guide techniques, which can make the space of template filled effectively, So that the template structure is accurately reproduced, experimental steps are as follows [8].

(1) The copper sheet were cut into 15 mm × 15 mm size, soaked into acetone for 3 min, remove impurities on the copper surface, cleaned in ultrasonic cleaning machine, washed with deionized water, dried by nitrogen.

(2) The copper plates were placed on the beaker accommodating polystyrene colloidal microspheres. The pressure of the gas-liquid interface is increasing slowly to the optimal pressure (18 mN / m). Copper plate previously immersed in a liquid can be pulled up by software controlling variable speed motor, polystyrene microspheres on water surface can be transferred to the copper plate. Its morphology was shown in Figure 5, average diameter of polystyrene microspheres is about 722nm.

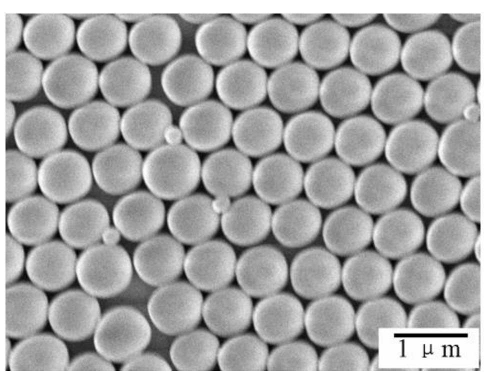


Figure 5. SEM Image of Template

(3) The electrolyte was 0.1 mol/L of CuSO4 solution (Beijing Chemical Plant), electrodeposition experiments completed by the electrochemical workstation (Wuhan Gaoss Union Company), deposition potential is about -0.5 V, deposition time was respectively 1s, 3s, 5s, 7s, 9s, 11s, 13s, 15s, 17s, 19s, 21s, 23s. Electrodeposition was finished, copper plates were cleaned by chloroform (Beijing Chemical Plant), removed polystyrene microspheres. When deposition time is 19 s, SEM images was shown in Figure 6.

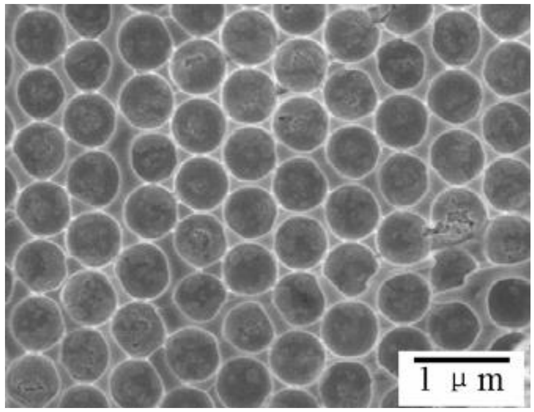


Figure 6. SEM Images of Macroporous Copper Films

4.2. Low Surface Energy Modification

Copper plate completed electrodeposition immersed into methanol solution of the pre-hydrolysis C8F13H4Si of 1.0wt.%. Soaked for 5 hours at room temperature, placed into the oven (202-3AB type, Tianjin Taisite Company), heated for 1 hour at a temperature of 130 ° C.

4.3. Contact Angle Measurement

Contact angle of copper plate completed prepared was measured by contact angle meter (DSA100, accuracy of 0.1°, made by KRUSS). the volume of water droplets was 5μL among experiments, each values of contact angle was measured for 5 times, Taking their average, which was 156.3°.

4.4. Effect on the Contact Angle of Microsphere Diameter

As can be seen from Figure 5(a), each polystyrene microspheres with around slits formed a unit, which is approximate a regular hexagon with inscribed microspheres. After electrodeposited, microspheres removed, diameter of spherical cavity is smaller than microspheres on the template (722 nm). f_s was calculated for example spherical cavity in Fig. 5(b).

$$f_s = \frac{A_0 - A_h}{A_0} = 1 - \frac{A_h}{A_0} \tag{2}$$

In Eq.2, A_0 is the area of the microspheres around slits, $A_0 = 451431.9$. A_h is the area of microspheres cavity, $A_h = 301754nm^2$. A_0, A_h are brought into Eq.2, get $f_s = 0.33$, contact angle of copper surface is θ, $\theta = 82.5^\circ$, f_s and θ are brought into Eq.1, obtain $\theta_c = 128.8°$

Surface free energy of copper experimental samples can be reduced through fluorine silane modified, which of contact angle is 156.3 °, the performance of super-hydrophobic.

4.5. Effect on the Contact Angle of Deposition Time

The contact angle is increasing with the deposition time. When the deposition time is 19s, the contact angle is the maximum. When electrodeposition time is greater than 19s, the contact angle starts to become smaller, the process of contact angle changing with deposition time process is shown in Figure 7.

In the deposition process, the thickness of the deposited layer is increasing with the deposition time, the depth of the spherical cavities is also increasing, f_s is decreasing, according to Eq.1, the contact angle of copper surface is increasing. If depth of spherical cavities continues to increase, f_s is increasing, according to Eq.1, the contact angle of copper surface is decreasing.

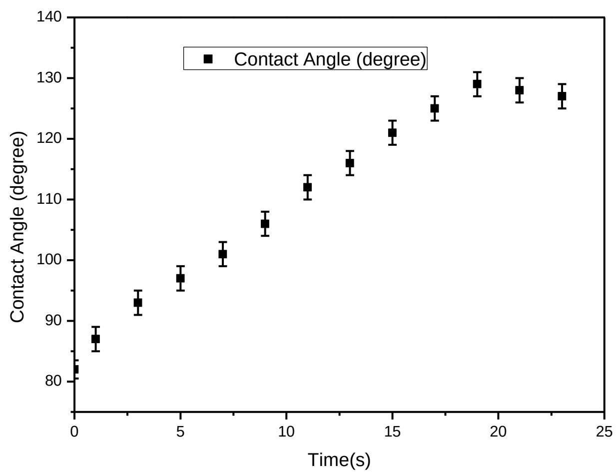


Figure 7. Curve of Contact Angle Changing with Deposition Time

5. Conclusion

(1) Microstructure of lotus leaves, canna leaves, reed leaves and bluegrass leaves were observed through electron microscopy, experiments show that micro-nano structures is an important factor caused surface with superhydrophobic property, different microstructure can obtain similar superhydrophobic effect.

(2) Experiment prepared template of polystyrene microspheres with 722nm diameter, copper atoms filled effectively the gap of template of polystyrene microspheres by electrodeposition method, the template was removed, the copper surface obtains regular array microstructure of spherical cave.

(3) The copper surface with spherical cave was modified by low surface energy material (fluorinesilane), the contact angle of copper surface is 156.3 °, which is superhydrophobic.

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