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Ceramics International 39 (2013) 8165–8172

CERAMICS INTERNATIONAL

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# Hydrophobic properties of biomorphic carbon surfaces prepared by sintering lotus leaves

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Received 17 January 2013; received in revised form 28 March 2013; accepted 29 March 2013
Available online 9 April 2013

## Abstract

Superhydrophobicity is a common characteristic of many plant leaf surfaces. In the present study, a superhydrophobic biomorphic carbon surface was fabricated by sintering a natural lotus leaf in argon and covering it with fluorine silane [(heptadecafluoro-1,1,2,2-tetradecyl) triethoxysilane]. After sintering, the carbon sample retained the surface structure of the lotus leaf with high fidelity. This carbon exhibited superhydrophobicity after it was covered with fluorine silane. The largest contact angle of water on this surface was 159°, which exceeds that on the lotus leaf (157°) and is much higher than that of smooth carbon covered with the same fluorine silane (114°).

*Keywords:* Sintering; Carbon; Lotus leaf; Superhydrophobicity

## 1. Introduction

Superhydrophobicity is observed in parts of many plants, including lotus leaves, rice leaves, rose petals, *Nasturtium* leaves, and peanut leaves. Water droplets, such as rain, remain unstable on top of the leaf surface, forming a spherical shape with a contact angle (CA) greater than 150°. They roll off quickly when subjected to gentle vibration, and wash away dust, imparting a self-cleaning function to the leaves. The surfaces of these plant leaves exhibit high static CAs of $>150°$ because of the combination of their micro-/nano-hierarchical structures with low-surface-energy wax coating [1–5]. Fig. 1 shows the microstructure of a lotus leaf. High-resolution imaging clearly reveals many micro-papillae with an average diameter of 5–9 μm and an average separation distance of nearly 12 μm. The surface of the papillae themselves is also rough, composed of branch-like nanopillars with an average diameter of 124 nm [4,5]. Water droplets on these surfaces readily remain on the apex of the nanostructures because air bubbles fill the valleys between the papillae under the droplet. The surface film on the leaf is mainly composed of C and O elements constituting an organic wax with a low surface energy [6]. Because of the combined effects of such hierarchical structures and the wax layer, water droplets usually bead up and effortlessly roll off. This superhydrophobic property is known as the “lotus effect” [1–5].

Superhydrophobic surfaces have many potential applications in daily life and industrial production [1,2,6–8]. Examples include self-cleaning windows, windshields, exterior paints for buildings and ships, utensils, roof tiles, textiles, solar panels, and micro- and nanofluidic applications requiring a reduction in fluid flow drag. Inspired by plant leaves, researchers have made many attempts to imitate the structure and composition of these leaves to obtain artificial superhydrophobic surfaces [9–14]. Superhydrophobic surfaces are usually prepared by constructing rough surface structures on the hydrophobic materials or by coating rough surfaces with low-surface-energy materials that often contain fluorine [15,16]. Different methods have been applied; these have included creating structured coatings similar to the lotus leaf from polyelectrolyte multilayer films [10], forming a gel-like porous coating using polypropylene, selecting suitable solvents and temperatures by which to control the surface roughness [11], and others [12–15]. However, most of these rough structures are

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http://dx.doi.org/10.1016/j.ceramint.2013.03.092

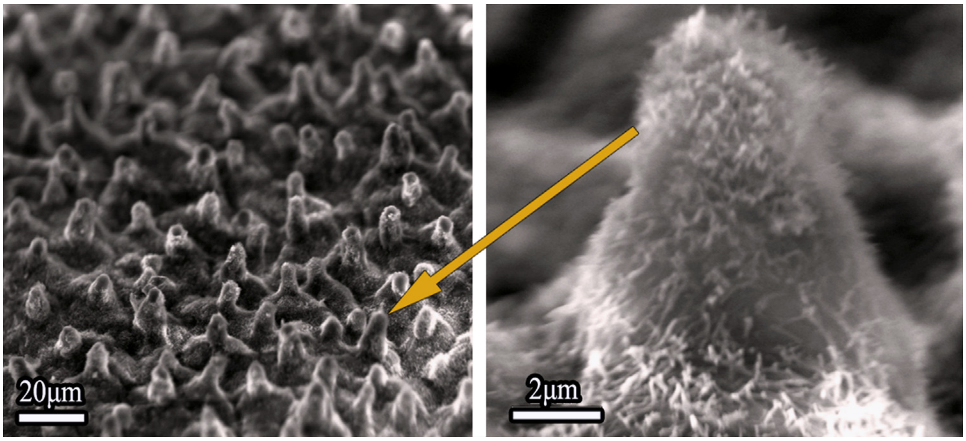

Fig. 1. Microstructures of a lotus leaf.

obtained by artificial imitation, and therefore, we cannot precisely mimic the fantastic inner structures of the hydrophobic leaves, which have developed over hundreds of millions of years, even by using the highest levels of technology and equipment. This limits the further improvement of the superhydrophobic properties of materials.

Since the past decade, the interest has grown in using biotemplates to prepare materials with bio-structures. Often superior to synthetic materials, natural materials such as wood, cotton, and jute possess fantastic structures with amazing functions and capabilities. Inspired by nature, researchers have selected bio-structures from different species to use as templates for synthesizing various desired ceramics such as SiC, TiC, $Al_2O_3$, and $SnO_2$. These products retain the microstructures of the original, natural materials, which are the key factors that provide the ceramic materials with excellent new properties [17–19]. This biotemplate method provides a new and effective way to fabricate materials with desired properties.

In this work, we present the preparation of a superhydrophobic carbon surface that is similar to the surface structure of a lotus leaf with high fidelity, by sintering a leaf as a template and covering the resulting carbon sample with a low-surface-energy material (fluorine silane). Then, the microstructure and the hydrophobicity of the obtained surface were investigated. If this carbon surface can inherit a structure similar to that of the lotus leaf, it may also exhibit the same superhydrophobicity as the lotus leaf.

## 2. Experimental

### 2.1. Materials and chemicals

Lotus leaves (picked from Xuanwu Lake, Nanjing); fluorine silane [FAS, (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane, provided by Xiamen Sicong New Materials Development Co., Ltd]; isopropyl alcohol (AR, provided by Sinopharm Chemical Regent Co., Ltd).

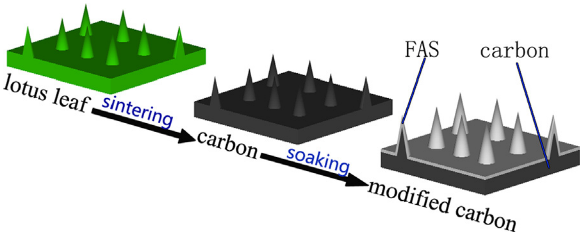

Fig. 2. Schematic diagram of the fabrication process of the superhydrophobic surface.

### 2.2. Preparation of superhydrophobic surface

Fig. 2 shows the fabrication process of the superhydrophobic surface. The lotus leaves were used as plant templates. They were laid in a drying box for 72 h at a temperature of 100 °C. The dried blades were sintered in a highly pure argon (Ar) atmosphere at a heating rate of 2 °C/min to 200 °C, and then to 800 °C at a rate of 1 °C/min, after which they were kept warm for 1 h. The leaves could be pyrolyzed into carbon after Ar-sintering [19]. Then, this biomorphic carbon was soaked in FAS with isopropanol (at a volume ratio of 1:5) for 1–30 days to obtain an FAS coating. Finally, the modified biomorphic carbon was placed in air for 1–2 days to dry naturally.

### 2.3. Characterization

A field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) was used to characterize the surface microstructures of the unmodified and modified biomorphic carbon, and the elements on these surfaces were examined using an energy dispersive spectrometer (EDS). The distribution states of F and Si elements were studied with an environmental scanning electron microscope (XL-30ESEM, Philips). A Fourier transform infrared (FT-IR) spectrometer (55FT-IR, Germany) was applied to analyze the chemical bond structure. The water CAs were measured with a contact angle measurement instrument (JC2000D2, Shanghai Zhongchen

Digital Technology Apparatus Co., Ltd) with a distilled water droplet volume of 2 μL. A water droplet of 2 μL was pushed down and released on the surface. Then, an optical camera captured the shape of the droplet on the surface, from which the CA was measured. In order to establish a reference CA value for comparison with the modified carbon, a flat and smooth surface was prepared by grinding and polishing a mass of carbon. This carbon surface was also immersed in the same FAS as that used for the modified carbon. We measured the water CA of the droplet on this modified surface as well as on biomorphic carbon.

## 3. Results and discussion

### 3.1. Macrostructure

Fig. 3a shows a full-scale picture of a fresh lotus leaf. Water forms a nearly spherical droplet on its surface, as shown in the inset. Fig. 3b and c shows the dried leaf before and after sintering. The carbon sample maintained the macroscale structure of the leaf well, even including the slim veins in the lotus leaf.

### 3.2. Surface morphology and composition analysis

Fig. 4a shows the surface microstructure of the unmodified biomorphic carbon obtained by sintering a lotus leaf in Ar. Compared with the microstructure of the lotus leaf in Fig. 1, the microstructure of the carbon is similar, with small papillae. The average diameter of the small hills is approximately 6–15 μm, and the average distance between two hills is 5–9 μm. Higher magnification reveals that these hills are textured with intricate nanostructures, as shown in the further magnification. Thus, the carbon sample retained with high fidelity not only the microstructure of the leaf but also its fine nanoscale structure. It is supposed that the mixed biopolymers in the leaf decomposed into carbon and gases during the sintering in Ar, giving rise to biomorphic carbon with a morphology derived from the leaf template [19]. However, the microstructure of the leaf surface was not damaged during sintering, and it was successfully transferred to the biomorphic carbon. Note that all the biomorphic carbon that we prepared showed high fidelity with this morphology, and the replication process is easy to control.

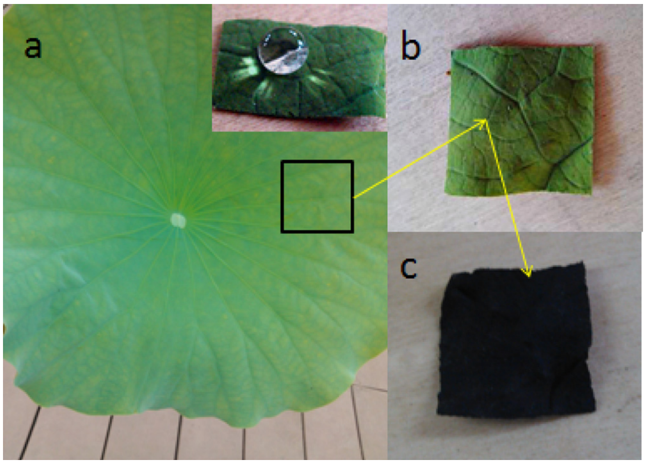

Fig. 3. Full-scale pictures of (a) a fresh lotus leaf with inset to show water droplet on its surface, (b) dried lotus leaf, and (c) carbon derived from the lotus leaf.

Fig. 4b and c shows the surface microstructures of the biomorphic carbon modified by soaking it in FAS for 1 day and 25 days, respectively. Fig. 4d shows the EDS spectra of the surfaces of the unmodified carbon and modified carbon. From these spectra, we can clearly see that the unmodified carbon mainly contains C and O elements. However, after the carbon is immersed in FAS, the surface develops F and Si peaks. This indicates that FAS covered the surfaces of the modified carbon. From their microstructures shown in Fig. 4b and c, we can see that the modified carbon retains the original leaf morphology well. It can be confirmed that FAS covered the surface of the biomorphic carbon much like a coating. The higher-magnification image of Fig. 4b shows that the tops of the convex cell papillae are also rough, featuring sub-micrometer-sized asperities whose average diameter is 100 nm and whose shape is similar to the nanostructures observed in Fig. 1. The tops of the papillae presented flower-like aggregates when the carbon was soaked for 25 days (Fig. 4c). The diameter of these “flowers” is in the range of several micrometers with sub-micrometer sized “petals” radiating from the center.

According to the FESEM and EDS data, FAS surface treatment had almost no effect on the biomorphic carbon microstructure. The surface treatment merely generates a thin silane layer on the substrate, thereby changing its chemical properties. The distribution of F and Si on the modified biomorphic carbon surfaces as a function of soaking time is given in Fig. 5. By comparing the two images, we can draw the conclusion that surface coverage improves with soaking time. After soaking for 25 days (Fig. 5b), the coverage of F and Si is greater than that obtained after soaking for 1 day (Fig. 5a). This indicates that extended soaking time is required to obtain full coverage of the surface with FAS.

### 3.3. Modification mechanism

In order to further clarify the chemical bonding in the modified biomorphic carbon, the samples were studied by FT-IR spectroscopy over the wavenumber range of 500–4000 cm$^{-1}$. The results are shown in Fig. 6, and the insets are enlarged graphs of the corresponding curves in the range of 1000–1500 cm$^{-1}$. In the modified carbon sample, the disappearance of the C–H stretching peak at 2976 cm$^{-1}$, corresponding to methyl or methylene groups, and the peak at 1467 cm$^{-1}$ corresponding to $CH_3$ or $CH_2$ deformations, demonstrates that the FAS has fully hydrolyzed.

Comparison with the IR spectra of unmodified carbon shows that the surface after chemical modification develops three new peaks at 1397 cm$^{-1}$, 1196 cm$^{-1}$, and 1108 cm$^{-1}$. These, respectively, correspond to stretching vibrations in $CF_3$, $CF_2$, and Si–O–Si. This indicates that after chemical modification, FAS forms a

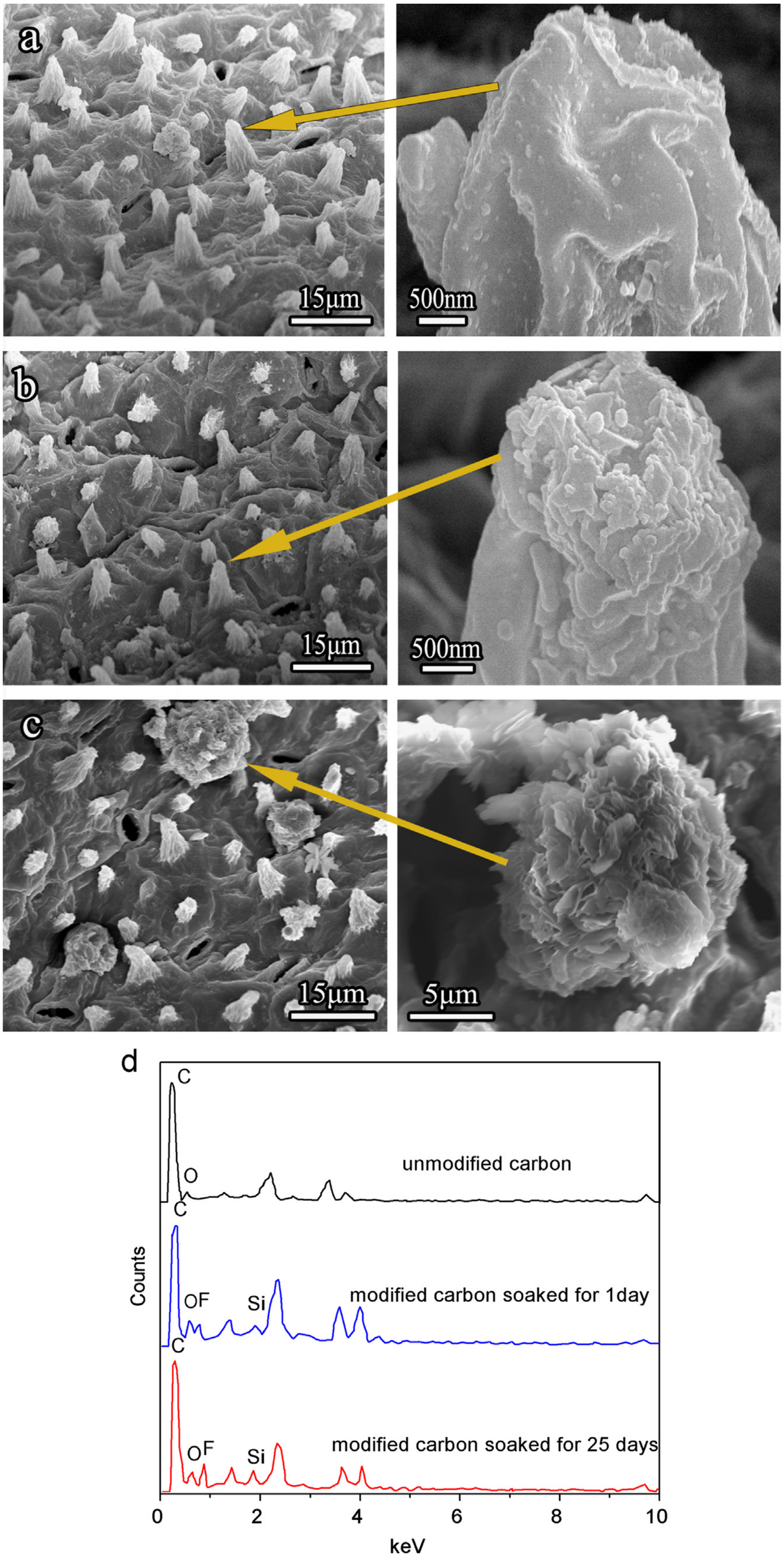

Fig. 4. FESEM images of (a) the unmodified biomorphic carbon, the modified biomorphic carbon soaked for (b) 1 day and (c) 25 days, and (d) the EDS spectra of the materials in these figures.

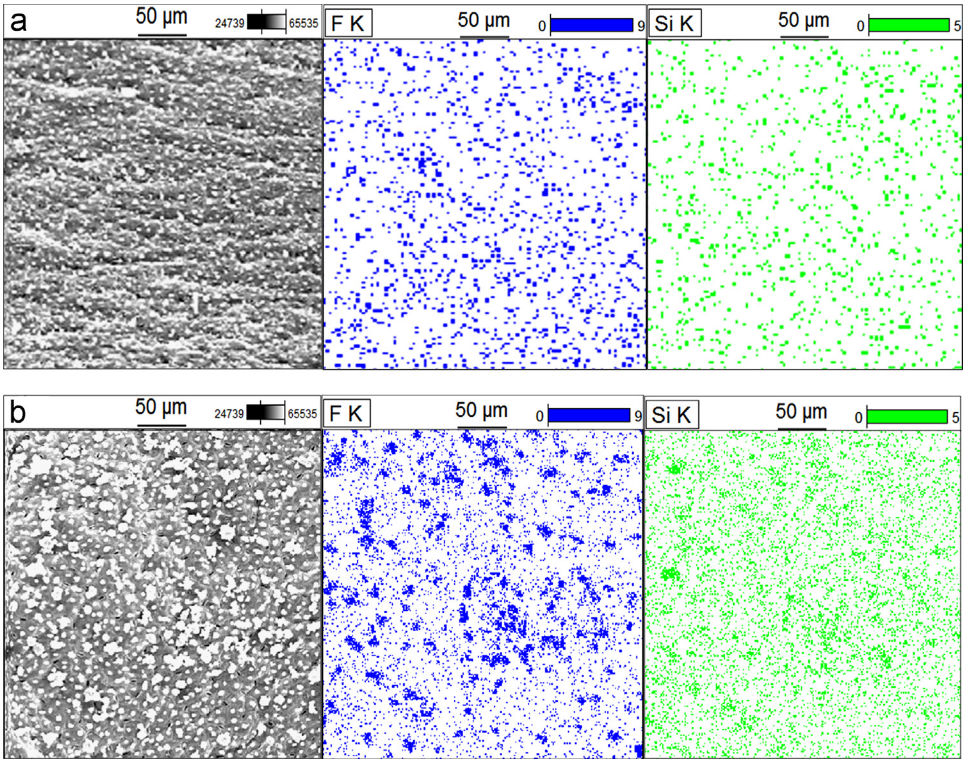

Fig. 5. The distribution of F and Si on the surfaces of the modified biomorphic carbon soaked for (a) 1 day and (b) 25 days.

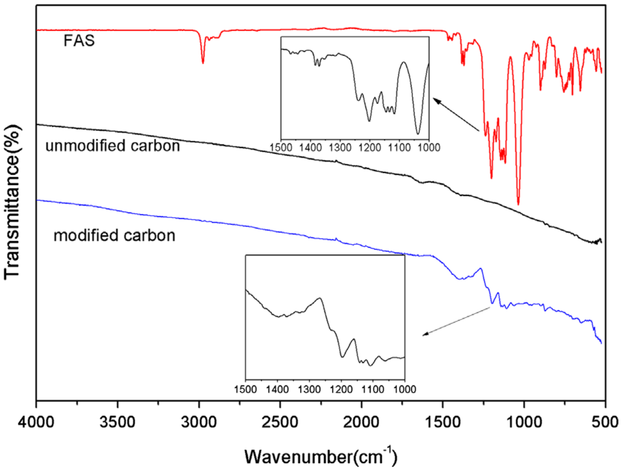

Fig. 6. FT-IR spectra of the materials of FAS, unmodified carbon, and modified carbon.

self-assembled monolayer on the carbon surface through hydrolysis and polycondensation. The hydrophobic groups of FAS are critical to lowering the free energy of the carbon ceramic surface.

### 3.4. Superhydrophobic properties

Fig. 7 shows images of water droplets on several different surfaces. The water CAs of the modified biomorphic carbon soaked in FAS for 1, 4, 5, 6, 15, 25, and 30 days are, respectively, 136, 140, 154, 157, 158, 159, and 157°, as shown in Fig. 7b–h. Up to a soaking time of 5 days, the water CA increases with soaking time. In other words, 5 days is the minimum time for the appearance of a 150° CA, characteristic of superhydrophobicity. However, there are only a few CAs above 150°. With an increase in soaking time past 5 days, the CA stabilizes; from the 6th to 30th day, the CA varied between 157° and 159°.

From Fig. 7d–h, we can see that the water CA of the modified biomorphic carbon soaked for greater than 5 days are approaches or exceeds that of the lotus leaf (157°, Fig. 7a). The biomorphic carbon with low-surface-energy coating therefore possesses superhydrophobicity similar to that of the lotus leaf. For reference, a CA value of only 114° was measured on a modified smooth carbon surface with no micro- or nanoscale structures (Fig. 7j). Researchers have reported that the CA of water on a smooth surface cannot exceed 120°, and that hydrophobicity can be enhanced by surface roughness [20–30]. The superior hydrophobicity of the modified biomorphic carbon compared to the smooth one can therefore be attributed the topography of the leaf-like carbon. As for the unmodified biomorphic carbon, the water cannot form a droplet on its surface; instead, the water spreads out quickly, as shown in Fig. 7k. The water CA of this surface is only 23°, indicating that the biomorphic carbon without a low-surface-energy coating is highly hydrophilic. From these CA results, we can see that the two above mentioned surfaces in Fig. 7b–h and k were covered by the same FAS, but show different hydrophobicities. That is to say, the surface geometry has a significant effect on the hydrophobicity of a material. Moreover, although the two surfaces in Fig. 7b–h and a have the same geometry, they still exhibit different wetting properties. That is to say, the chemical composition of the surface can also

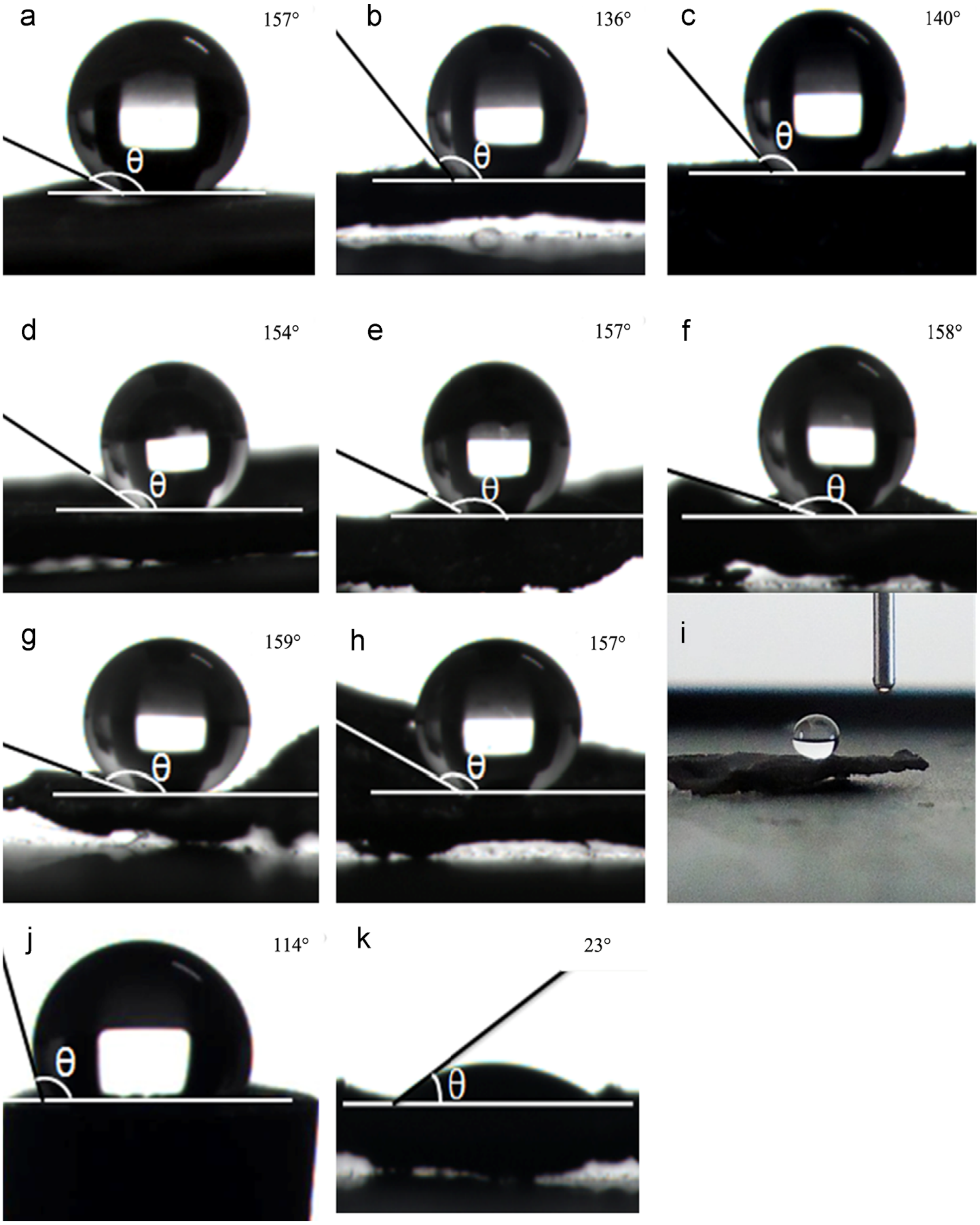

Fig. 7. Micro-photographs of water CA of (a) the lotus leaf (157°), (b–h) the modified biomorphic carbon soaked for 1 day (136°), 4 days (140°), 5 days (154°), 6 days (157°), 15 days (158°), 25 days (159°), and 30 days (157°), respectively, (i) Macro-photograph of droplet on the modified biomorphic surface, (j) modified smooth carbon (114°), and (k) the unmodified biomorphic carbon (23°).

affect the hydrophobicity. It is known that the wetting properties of a surface depend on both its chemical composition and surface morphology [31]. Artificial superhydrophobic surfaces are made by creating coarse textures on hydrophobic materials, or by first creating coarse textures on a hydrophilic material and then covering it with a hydrophobic coating [32,33,9,10]. The lotus leaf also grows in this manner; that is, by depositing a wax onto the micro- and nanostructured surface of its leaves, it produces leaves whose surface exhibits superhydrophobicity [9]. In this study, we cover biomorphic carbon with FAS to imitate the natural geometry and chemical composition of superhydrophobic lotus leaves.

In addition, the samples display good hydrophobic performance stability: they maintain superhydrophobicity after several months at room temperature. From Fig. 7i, we can see that the water droplet is almost a sphere on the modified surface. Its CA reaches 159°.

As more air is trapped between the water droplet and the carbon surface, it prevents complete wetting of the surface, resulting in a higher CA. This wetting mechanism can be explained by the Cassie model [34]:

$$cos\theta^* = (1-f)(cos\theta + 1) - 1,$$

where $\theta^*$ and $\theta$ are the CAs on rough and smooth carbon surfaces, respectively, and $f$ is the area fraction of air trapped in the surface. Putting the CAs of Fig. 7b–h into the formula, we calculate that $f = 0.53$, 0.61, 0.83, 0.87, 0.88, 0.89, and 0.87, respectively. When $f$ is below 80% on account of a short soaking time, the contact area of water with the modified surface is relatively large and the angle is less than 150°, as shown in Fig. 7b–c. With an extension of the soaking time, the carbon surface becomes more hydrophobic as it is covered with more fluorinated silane (as explained by Fig. 5), and more air is trapped in between the micro- and nanoscaled structures. When nearly 90% of the modified surface is filled by air, water sits on such a surface much like it would on an air cushion, only forming several contact points with the convex top. As a result, the water repellency is dramatically enhanced, as shown in Fig. 7d–h.

Here, a carbon surface that retains the leaf structure with high fidelity is easy to fabricate by sintering the leaf. Further research can focus on using more plant leaves, such as rice and indicalamus leaves, to prepare more ceramics such as ZnO, TiC, $TiO_2$, SiC, $SiO_2$, and $Al_2O_3$. This can be done by immersing biomorphic carbon in special solutions that include $Zn^{2+}$, $Ti^{4+}$, $Al^{3+}$, or Si, drying it, and sintering it.

## 4. Conclusions

Superhydrophobicity is observed in parts of many plants. This unique property benefits from the presence of a hydrophobic wax layer covering their micro- and nanostructured surfaces.

In this study, a superhydrophobic biomorphic carbon surface that is similar to the surface structure of a lotus leaf with high fidelity was fabricated by sintering a leaf as a template and covering the resulting carbon with FAS. The microstructure of the leaf surface was not damaged during sintering and was successfully transferred to biomorphic carbon. In addition, we covered this biomorphic carbon with FAS to imitate the chemical composition as well as the natural geometry. The modified carbon surface exhibited excellent superhydrophobic properties. Its highest water CA is 159°, which is greater than that of the lotus leaf.

Compared with artificial imitation or other preparation, this approach is not only easy to control but also can be used to prepare superhydrophobic surfaces with high fidelity to the structure of plant leaves. The present study suggests that this method of sintering the leaf template can provide a new way to fabricate superhydrophobic surfaces.

## Acknowledgments

The authors wish to express thanks to National Natural Science Foundation of China (No. 51002077), Foundation of “Zijin Star” of “Excellence Program” of NJUST, and Scientific Research Foundation for the returnee of Ministry of Education of China.

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