# ARTIFICIAL LOTUS LEAF STRUCTURES MADE BY BLASTING WITH SODIUM BICARBONATE

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## 1 Introduction

It is generally recognized that surfaces having a contact angle (CA) of greater than 150° are superhydrophobic surfaces. Many researches have shown that superhydrophobic surfaces can be made of dual scale structures which consist of hierarchical micrometer- and nanometer-sized structures, like those on the lotus leaf. [1-3]. These surface was obtained from enhancing surface roughness, especially by the self-assembly of a monolayer [4], photolithography [5, 6], plasma polymerization [7], UV illumination [8], electrospinning [9], ion irradiation [10,11], template methods [12-17], and chemical deposition [18-20]. The CA hysteresis is defined as the difference between the advancing and the receding CAs. If Superhydrophobic surfaces feature low CA hysteresis, these surface will have water repellent, self-cleaning, and low drag for fluid flow. Recently Bharat reported that the CA and CA hysteresis of hierarchical surfaces become higher and lower respectively than those of surfaces with nano structures [21]. This research emphasized the need of fabricating the hierarchical surfaces with a low CA hysteresis to apply to self-cleaning windows and exterior paints for buildings and ships.

Previously Lei et al. have reported that the hierarchical micrometer- and nanometer-sized structures can be fabricated from a micro-and nano-scale hierarchical template which was obtained from pressing 20-mm glass spheres into an Al foil and anodizing the dimpled Al foil. By replicating it, they were able to make dual-scale structure such as the lotus-leaf-like structures [12]. On the other hand, Kim et al. made the template by sandblasting with 50mm particles onto an Al plate and anodizing the sandblasted plate. However, these methods require the processes including delicate, time-consuming method and they are limited in the size. Especially, for template to obtain superhydrophobic surfaces by replication, the microparticles have to be removed from the nanoporous template. Therefore, it is required to fabricate uniformly superhydrophobic surfaces with hierarchical structures by a simple and cost-effective method.

Anodic Al oxide (AAO) is suitable material for replication of a porous AAO template because its pore dimensions and pore density can be easily adjusted by changing the anodizing conditions [22-25]. By replicating a AAO template, Super-hydrophobic surfaces have been obtained [26].

In this work, we report here the economical and practical method to fabricatie superhydrophobic micro-nano hierarchical structures; that is organized with blasting an Al foil (99.5%) by sodium bicarbonate and anodizing the Al foil. Because sodium bicarbonate is soluble in water well, it is easy to remove it used in blasting from the Al. And it is also cheap material relatively. Thus the method we proposed has distinctive advantages of cost-effective and expediency over conventional methods.

## 2 Experimental details

### 2.1 Fabrication of alumina template and its replica

The hierarchical superhydrophobic structure is fabricated using following mehods (see Fig. 1(a)).

First, microstructures were fabricated by blasting an Al foil with sodium bicarbonate using compressed air. Specifically the compressed air of which pressure is 6kgf $cm^2$ and the sodium bicarbonate

whose size is 25-30mm are used in this step. Bicarbonate-blasted AAO was fabricated through the anodization of an industrial Al foil (99.5%, 60 mm × 40 mm × 0.3 mm), using oxalic acid. Different bicarbonate-blasted Al foils were anodized for 0, 2, 3 and 4 min in a 0.3 M oxalic acid solution at a constant voltage of 40 V. To make nanoholes

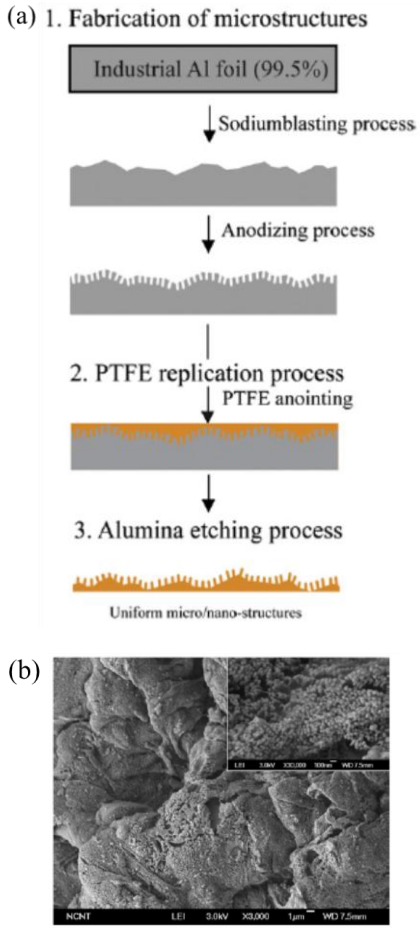


Fig.1 (a) Schematic representation to fabricate hierarchical superhydrophobic structures: first, sodiumblasting porous alumina template; then, PTFE replication and alumina etching in AZ 300 MIF. (b) SEM images of a sodiumblasted porous alumina PTFE replica with uniform superhydrophobicity.

widened, the AAO template was immersed in a 0.1 M phosphoric acid solution at a temperature of 25° C for 60 min. The nanoporous AAO prepared by this process was used as the replication template. In addition, a polymer replica was prepared by rubbing a PTFE solution (Polytetrafluoroethylene, Teflon® AF 601S2, 6 wt%, DupontTM) onto the replication template. After the curing process, the solvent was evaporated to leave a PTFE thin film. Finally, the micro-nano hierarchical structures were obtained after removal of the AAO template with an AZ 300 MIF developer. Fig. 1 (b) is the scanning electron microscopy (SEM) image of the replica which shows the nanofibers that had been replicated successfully on the micro-roughened structure.

### 2.2 Surface measurements

The contact angle (CA) of the replicated superhydrophobic surface was measured by using a Drop Shape Analysis system (DSA-100, Kruss Co.). And the dynamic advancing and receding CAs were recorded as the surface pushed and pulled [9]. For the purpose of doing this, we used a 3-μl droplet of distilled water. The average value was achieved from at least ten measurements made on different specimens at room temperature. SEM images were obtained using a field-emission scanning electron microscope under an accelerating voltage of 5 kV (FE-SEM, JEOL JSM-7401F, NCNT).

## 3 Results and discussion

We observed the surface morphologies of the aluminum and the porous aluminum they were blasted with sodium using SEM (Fig. 2). Fig. 2 (a) is the aluminum surface roughened by sodiumblasting. Fig. 2 (b) shows the porous alumina surface treated with the sodiumblasting and anodization. From the equation (1), the depth is expected to be about 350nm when the anodization time is 4min. The aluminum is anodized for 0, 2, and 3 min and their pore sizes are 0, 100 and 220 nm respectively. The aluminum has varying pore sizes because of using the industrial aluminum [17] and its mean pore size is about 40nm as shown in Fig. 2 (c)

Fig. 3 shows SEM images of PTFE replica structures which were replicated from the bicarbonate-blasted porous alumina. These are shown in Fig. 3 (a)-(d) specifically. The dual-scale hierarchical structures of which anodizing times are 0, 2, 3, and 4 min have a mean nanofiber measured 0, 100, 220, and 350 nm respectively. Owing to the trapped air in the dual-scale hierarchical structures, the actual contact area between the surface and droplet is reduced. For this

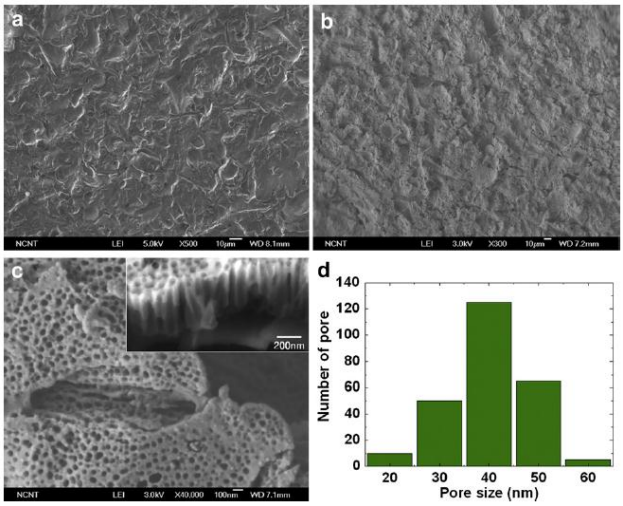


Fig. 2. SEM images of sandblasted aluminum and sandblasted porous alumina. (a) sodiumblasted aluminum surface, (b) sodiumblasted porous alumina surface, (c) sodiumblasted porous alumina surface with the anodizing time of 4 min. Inset show the cross-sectional image (d) Pore size distribution of the sodiumblasted porous surface with the anodizing time of 4 min.

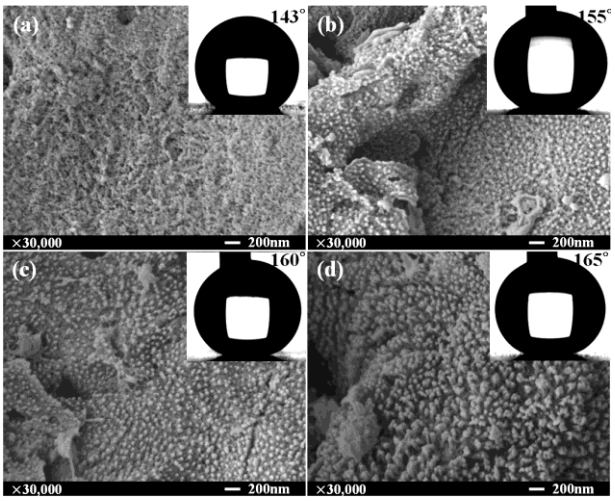


Fig.3. SEM image of the replicated hierarchical structures with varying anodizing time (a) 0 min (b) 2 min (c) 3 min (d) 4 min. Insets (a)-(d) show the apparent advancing contact angle for the specimens.

reason, the strong superhydrophobicity appears in the structure. The insets in Fig show the apparent advancing CAs of the dual-scale structure, 143° , 155° , 160° and 165° respectively. These CAs are averaged value.

The advancing and receding CAs on the dual-scale structure with nanofibers of which mean length 0, 220, and 350nm were measured. The Fig. 4 indicates that the apparent advancing CA increases and the CA hysteresis decreases as the mean length increases. That is, the trapped air in the dual-scale structure increases when the mean length of nanofiber increases. But the actual contact area between the surface and the droplet decreases. Because the dual-scale structure is impervious to water droplets, the structure shows a low value of contact angle hysteresis. For instance, the structure with 350nm nanofibers has a contact angle hysteresis of 3° . These both static and dynamic contact angle are almost identical to those of the Lotus leaf.

To investigate the aging effects in the air and water of the dual-scale nanofiber structure, the apparent advancing CA of them whose anodizing time was 4 min was measured for 3 months using 3-μl water droplets. The nanofiber structure was not influenced by aging in air and water, as shown in Fig. 5

## 4 Conclusions

In summary, we have successfully fabricated hierarchical structures with the dual-scale roughness. To make the surface having uniform superhydrophobicity, we used blasting and anodizing the Al foil. Sodium bicarbonate used in blasting is a low-cost material, which is soluble in water easily. Thus, we can remove easily the blasted particles from the surface while being anodized. This method to fabricate the dual-scale structure is simple and very inexpensive as compared to conventional methods like chemical deposition.

In addition, higher CAs and lower CA hysteresis can be obtained by increasing the length of nanofibers of the fabricated hierarchical structures. Therefore, this fabrication method makes it possible to design more robust nonwetting surfaces. The fabricated dual-scale structure similar to the lotus leaf can be applied to the wide range of applications from microfluidic devices for biological studies to industrial self-cleaning products for automobiles and ships.

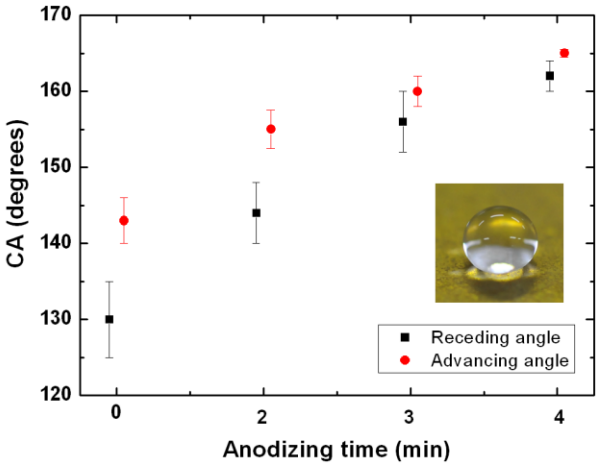


Fig.4. CA hysteresis for each specimen. The inset shows a virtually ball-shaped water droplet on superhydrophobic hierarchical structures.

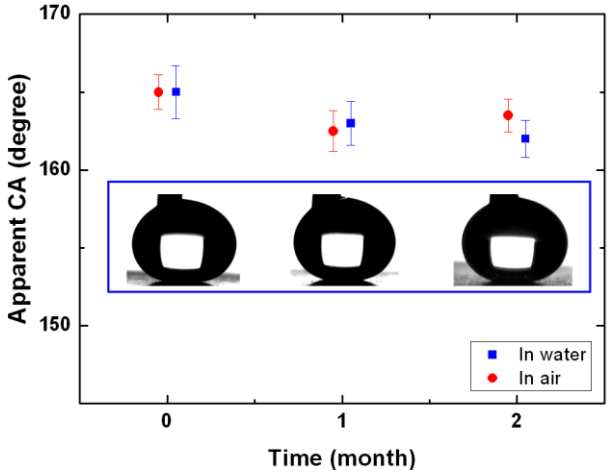


Fig.5. Aging effect on contact angles of the hierarchical superhydorphobic structure (anodizing time of 4min).

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