SUPERHYDROPHOBIC NANO/MICRO STRUCTURES BASED ON NANOHONEYCOMB

Donghyun Kim* Joonwon Kim*, Hyun C. Park*, Kun –H. Lee, and Woonbong Hwang***
***Dept. of Mechanical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Republic of Korea,**
****Dept. of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Republic of Korea.**

Keywords: *Nanohoneycomb, AAO, Superhydrophobic, Sandblast, Lotus Leaf, Replication, wettability*

Abstract

A surface was created with the same superhydrophobic property as the lotus leaf (Lotus Effect) by dipping of sandblasted porous alumina into polytetrafluoroethylene (PTFE, Teflon®: DuPont™) solution. The fabricated artificial lotus leaf had PTFE micro/nanostructures. This fabrication process has several advantages, including low fabrication cost, simplicity and easy coverage of a large area. The sandblasted porous alumina template was fabricated by sand blasting of aluminum sheet and anodization in oxalic acid. To obtain PTFE micro/nanostructures, PTFE replication based on the dipping method was used, with a 0.3 w% PTFE solution. To remove the aluminum and alumina layers, wet etching by chromic and phosphoric acid mixed solution and liquid $HgCl_2$ solution was used. The fabricated surface has a superhydrophobic property whose apparent contact angle of the PTFE micro/nanostructures was approximately 165° and sliding angle is less than 1°.

1 Introduction

The wetting of solid surfaces has been widely studied recently; wetting phenomena depend on the free energy and the geometry of surface structures [1,2]. Superhydrophobic materials such as lotus leaves have been studied both theoretically and experimentally [3,4] and there are many works covering their fabrication and properties [5,6]. In the present work, a superhydrophobic micro and nanostructures made by dipping method was fabricated on the sandblasted anodized porous alumina.

Anodic aluminum oxide (AAO) has been proposed as a suitable material for use in the burgeoning field of nanotechnology. In particular, porous type AAO has been used as a "***nanohoneycomb***" structured template for use in the fabrication of nanostructures. Anodic aluminum oxide (AAO) can be fabricated by electrochemical etching on an aluminum sheet in electrolyte solutions such as oxalic, sulfuric, and phosphoric acid solution [7-9].

2 Experimental Sections

2.1 Preparation of Treated Al Surfaces and Replica

We began with industrial grade aluminum (99.5 %) sheets (50 mm x 40 mm x 1 mm). We prepared 500 mesh (i.e., 50 μm in diameter) sand particles. The sand particles are ejected from a nozzle using compressed air. The pressure of the compressed air is 6 kgf/cm^2 and the sandblasting step is reciprocated 20 times. After sand blasting, the aluminum sheet is cleaned for next process by dipping in acetone for ten minutes and rinsed with deionized water.

The next step is anodization, which was carried out in 0.3 M oxalic acid solution. The sandblasted aluminum sheet was used as the anode, and a flat platinum sheet as the cathode. The electrodes were about 5 cm apart. A potential difference of 40 V_{DC} was applied by a computer-interfaced power supply (Digital Electronics Co., DRP-92001DUS). The sandblasted aluminum sheet was anodized for 10 minutes.

The next step is the replication. The anodized porous alumina was used as the template material. To make a polymer replica, the dipping method was used [30] with the mixed solution of PTFE (0.3 wt%) and the solvent, which comprises a solution of PTFE (Teflon® AF 601S2, 6 wt%, DuPont™) in the solvent (perfluoro-compound FC-75®, MW=420, ACROS ORANICS Co.,). The template was dipped into the mixed solution with the depth of 2 mm, and cured at room temperature. During the curing process, the solvent of the mixed solution was evaporated, and PTFE thin film remained. The considerable thickness of PTFE thin film could be obtained by this process.

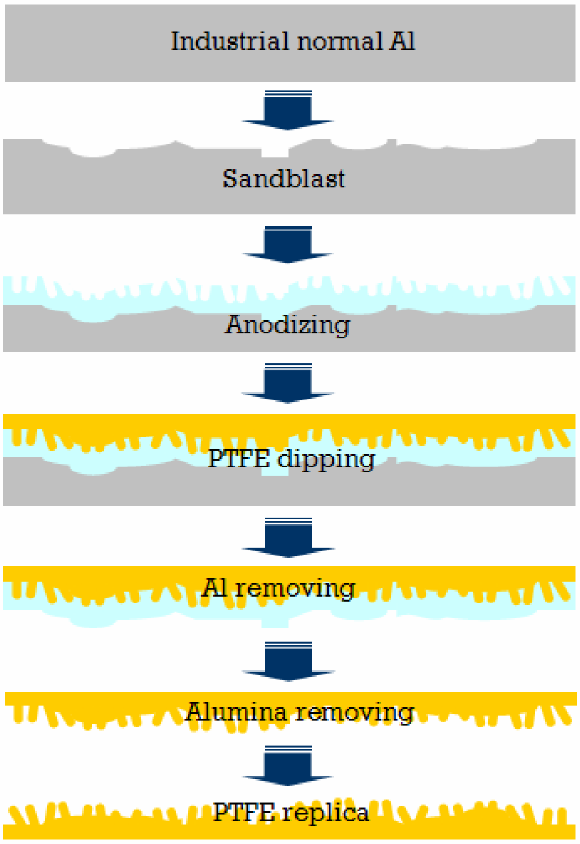

Fig. 1. Scheme for producing Sandblasted porous alumina PTFE replica structure

The final step is removal of the aluminum and alumina layers. The aluminum layer was removed in $HgCl_2$ solution. Residual porous alumina was then removed in a mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid at 65 ºC for 5 hours. Fig. 1 shows the overall scheme for preparing the PTFE replica.

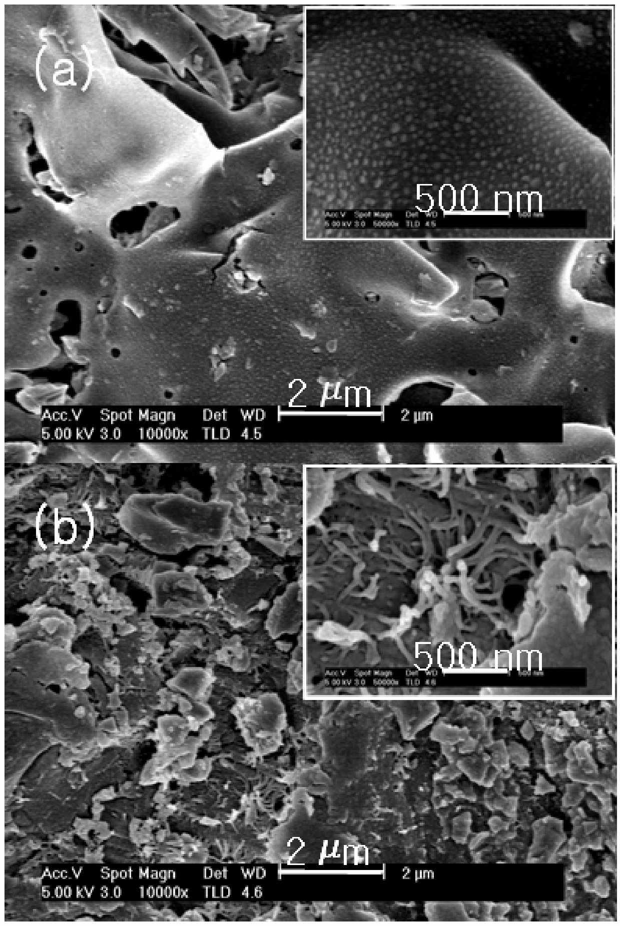

Fig. 2. Field-emission SEM surface images of the andblasted PTFE replica and the sandblasted porous alumina PTFE replica. (a) Sandblasted PTFE replica (b) Sandblated porous alumina PTFE replica

2.2 Surface Characterization

The sessile drop method, which measures the contact angle (CA) of a water droplet on a surface, was used to characterize the wetting properties of the resulting micro/nanostructures. A surface analyzer, DSA–100 (Krüss Co.), was used for the measurement. The samples were placed on a test stage and a water drop was introduced onto the surface through a microsyringe. Steady–state contact angles were measured using a 1 μL deionized water droplet. At least five different measurements were performed on different areas of each sample at room temperature. Contact angle measurements were performed on two types of samples: the sandblasted PTFE replica and the sandblasted porous alumina template PTFE replica. Flow resistance of water droplets is measured by the sliding angle test with DSA-100. The sliding angle the PTFE replica is measured with a 12 μL water droplet.

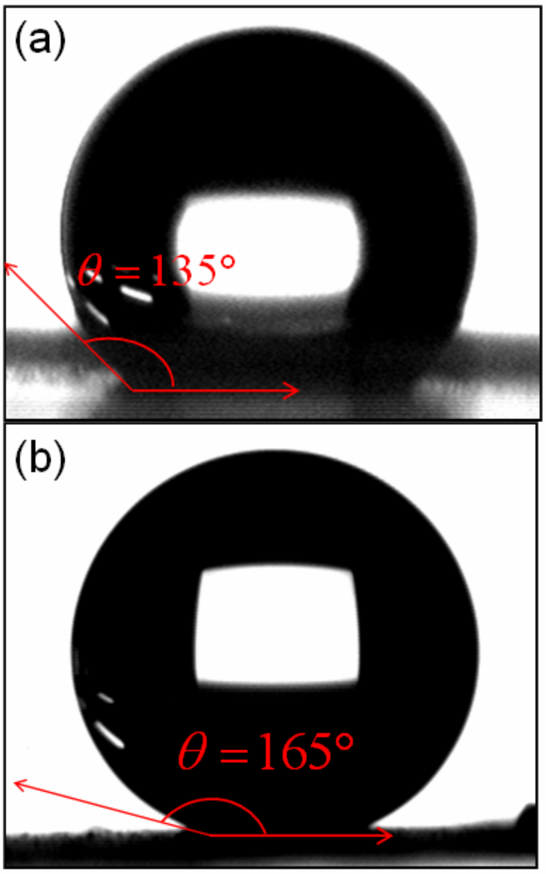

Fig. 3. Water droplets and contact angle (CA) on the surfaces shown in Fig. 2. (a) CA is 135° on the sandblasted PTFE replica surface shown in Fig. 2(a). (b) CA is 165° on the sandblasted porous alumina PTFE replica surface shown in Fig. 2(b)

3 Results and Discussion

3.1 Topography of the Treated Al Surface

To create PTFE micro/nanostructures, PTFE replication was made using the dipping method with a 0.3 wt% PTFE solution. To remove the aluminum and alumina layer, wet etching was performed using chromic and phosphoric acid mixed solution and HgCl2 solution. Fig. 2 shows the replicated PTFE structures from the sandblasted porous alumina template. Fig. 2(a) shows the sandblasted PTFE replica. These images verify the reliability of the sandblasted porous alumina PTFE replica. Fig. 2(b) is clearly distinct from Fig. 2(a). No nanoscale pillars exist in Fig. 2(a), but are present in Fig. 2 (b).

Fig. 2 (b) shows the SEM morphologies of the sp. 1 PTFE replica. The length of the pillars is about 1 μm, consistent with the relation between the anodizing time and the hole depth of the sandblasted porous alumina. This anodizing process altered the sandblasted aluminum surface to the porous alumina surface shown in Fig. 2(b), which exhibits hierarchical structures, having nanostructures on microstructures as on the lotus leaf.

3.2 Wetting Properties

Fig. 3 shows measured values of the contact angle. The contact angle of the sandblasted PTFE replica surface is 135º, as shown in Fig. 3(a). The intrinsic contact angle of PTFE is 120º, so that the microscale roughness of the surface increases the hydrophobicity. The sandblasted porous alumina PTFE replica surface has a contact angle of 165º (Fig. 3(b)). These were average values of the measured contact angle. The errors were less than 2º. We found that water droplets can not fix on the PTFE replica surface stably. The contact angle of fig. 3 (b) was taken when the droplets were fixed on the point with defect. This exhibits the superhydrophobic property. The nanoscale pillars dramatically reduce the contact area between the water droplet and the solid surface. The water droplets on these dual-scaled modified surfaces readily sit on the apex of the nanostructures, since air fills the space of the microstructures under a water droplet. A water droplet on these dual-scaled modified surfaces can not penetrate into the surface. This behavior is very similar to the superhydrophobicity of lotus leaves (the Lotus

Effect) [6]. A low sliding angle of water droplet is another important criterion used to determine a superhydrophobic surface. In fact, the rough hydrophobic surface with insufficient scale of projections can decrease the area of trapped air under a droplet that increases the sliding angle. Both large contact angle and low sliding angle should be considered for a surface with superhydrophobicity [9]. The sliding angle of PTFE replica surface that initiate droplet sliding was less than 1°. The droplet cannot be stabilized on the PTFE replica surface.

4 Conclusions

The superhydrophobic artificial lotus leaf has successfully been mimicked using inexpensive engineering materials and a simple fabrication processes. The first process is sandblasting, which generates micoscale roughness on the surface of an industrial grade aluminum sheet. The sandblasted aluminum surface was then anodized. The anodized aluminum oxide surface has nanoscale porosity. The resulting micro/nanostructures were like the reverse side of a lotus leaf. Finally, PTFE replication was performed using the dipping method. These processes generated a hierarchical structure with nanostructures on microstructures such as a lotus leaf. The fabricated PTFE replica exhibits permanent superhydrophobicity. The contact angle of the PTFE replica structures was approximately 165 ° and the sliding angle is less than 1°.

Acknowledgements

This research was supported by Grant No. R01-2006-000-10585-0 (2006) from the Korea Science and Engineering Foundation (KOSEF).

References

[1] Young T., “An Essay on the Cohesion of Fluids”, *Philosophical Transaction of the Royal Society of London*, 95, 65-87, 1805.

[2] Cassie A.B.D., Baxter S., “Wettability of Prous Surfaces”, *Trans. Faraday Soc.*, 40, 546, 1944.

[3] Marmur A., “Wetting on Hydrophobic Rough Surface: To Be Heterogeneous or Not To Be?”, *Langmuir*, 19, 8343-8348, 2003.

[4] Barthlott W., Neinhuis C., “Purity of the Scared Lotus, or Escape from Contamination in Biological Surfaces”, *Planta*, 202, 1-8, 1997.

[5] Zhai L., Cebeci F. Ç., Cohen R. E., and Rubner M. F., “Stable Superhydrophobic Coatings from Polyelectrolyte Multilayers”, *Nano Letters*, 4(7), 1349-1353, 2004.

[6] Fürstner R. and Barthlott W., “ Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces”, *Lanmuir*, 21, 956-961, 2005.

[7] Jessensky O., Müller F., Gösele U., “Self-Organized Formation of Hexagonal Pore Arrays in Anodic Alumina”, *J. Appl. Phys.*, 72, 1173, 1998.

[8] Masuda H. et al., "Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina, ", *Science*, 268, 1466 ~ 1468, 1995.

[9] Hwang S.K., Jeong S.H., Hwang H.Y., Lee O.J., Lee K.H., “Fabrication of Highly Ordered Pore Array in Anodic Aluminum Oxide”, *Korean J. Chem. Eng.*, 19(3), 467-473, 2002.