

Preparation of a Superhydrophobic Film on Micro Lens Arrays Pattern

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Superhydrophobic surface, characterized by water contact angles (CA) greater than 150° , have been attractive for various applications.¹⁻² Specifically, water repellence is useful dust-free coating, a covering that prevents snow from sticking to antennas and windows, and reduces the friction of water flow. It is known that the roughness of a hydrophobic surface increases its hydrophobic properties. Many plants, including the lotus leaf, naturally exhibit the unusual wetting with this kind of rough architecture. In particular, the surface of the lotus leaf consists of micron-sized hills bearing nanometer-sized wax particles with a very rough surface. The lotus leaf also has self-cleaning properties. Rolling water-droplets wash off contaminants and dust because the water drops sit partially on the rough surface. Various methods have been proposed to mimic the surface structure of the lotus leaf. They include porous structure, micro-patterned structure, and carbon nanotubes with a fluoroalkylsilane treatment. Although previous methods have demonstrated excellent superhydrophobicity,³⁻¹⁵ most of them have involved strict conditions, expensive material, or complicated procedures, such as etching and plasma treatment.²⁰⁻²⁷

Here we present a simple procedure for preparing a superhydrophobic film with the aid of a hemisphere pattern structure and a porous material. First, we used large porous silica particles because surfaces of silica particles can be modified easily with organo-silane and rough surface structures. These structures are useful for mimicking the micro-nano architecture of a lotus leaf. Porous silica particles of 1-3 μm (PSPs, Dongyang Chemical, ML381) were mixed with a conformal coating solution (Dow Corning, I-2577). The mixed solution was drawn on a poly(ethylene terephthalate) (PET) sheet with a manual applicator of about 5 μm wet film thickness and then cured at room temperature for 5 min. Conformal coatings are materials applied in thin layers onto electronic substrates. In solution, dimethyl methylphenylmethoxy siloxane was used as binder to merge particles onto surface and methyltrimethoxysilane was used as hydrophobic surface modifier. We measured the wettability of the film with water on the surface. As shown in the inset of Figure 1, the measured static water CA was $155 \pm 3^\circ$. While the CA of thin film coated without containing PSP was $90 \pm 5^\circ$. The surface wetting property of coated film was dramatically changed by adding porous particles. To investigate the effect of the surface structure on the film, the morphology of film was examined with the scanning electron microscope

(SEM).

The random rough surface structure was generated by the large particle size distribution (PSD) of porous particles as shown Figure 1. The particles generated micro structure and the papilla of it formed nano structure on the surface. Although thin films coated with porous particles showed a superhydrophobic surface at partial area, a large unwettable surface area was not obtained. The rolling-off water drop sometimes pinned on surfaces even small area (5 cm \times 5 cm) shown clearly by video clips. In order for not be pinned, superhydrophobic surfaces have to be small CA hysteresis (difference between advancing and receding CA) and it is more important in characterizing superhydrophobicity than the maximum achievable CA,¹⁶ so the dynamic water CA was measured. The measured advancing CA was $152.93 \pm 1.64^\circ$ and receding CA was $147.67 \pm 2.60^\circ$. The CA hysteresis was about 5° .

To imitate lotus leaf structure that has regular micro structure, we used a micro lens array (MLA) as a large pattern. MLAs are important in photonics and electronics applications, such as optical telecommunications and light homogenizers for liquid crystalline display (LCD). A simple way to produce MLAs is by using the regular shape of a molding. Once a suitable template is developed, positive MLAs films can be fabricated easily from negative molds.¹⁹ MLAs films with a 50 μm hemisphere pattern were generated from the negative Ni mold. The water CA on bare MLA films was $50 \pm 7^\circ$ and the CA of an MLA sheet coated with conformal solution was $110 \pm 5^\circ$.

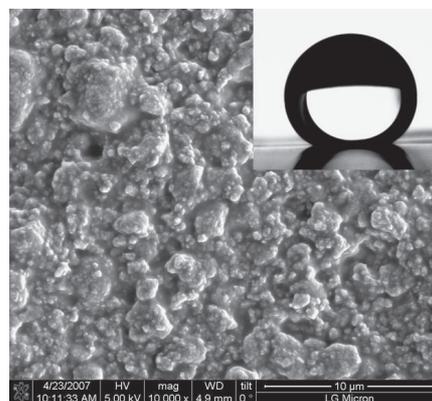


Figure 1. SEM images of PET film coated with porous silica particles. Inset is static contact angle on this surface.

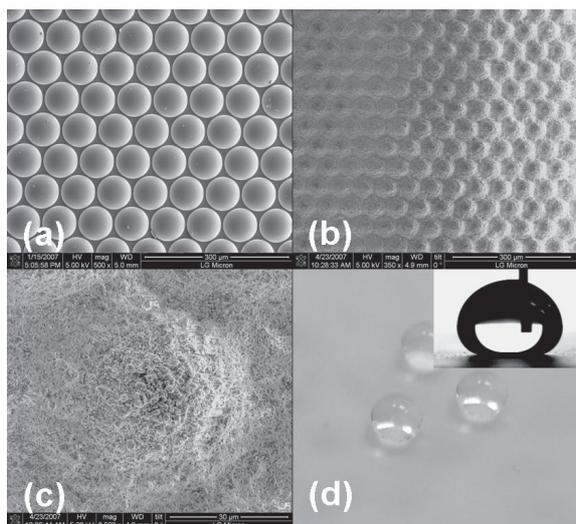


Figure 2. SEM images of MLA patterns coated with porous silica particles: (a) micro lens array pattern, (b) wide view of lens coated with porous silica particle, (c) narrow view of porous silica particle, (d) water drops and contact angle of superhydrophobic surface.

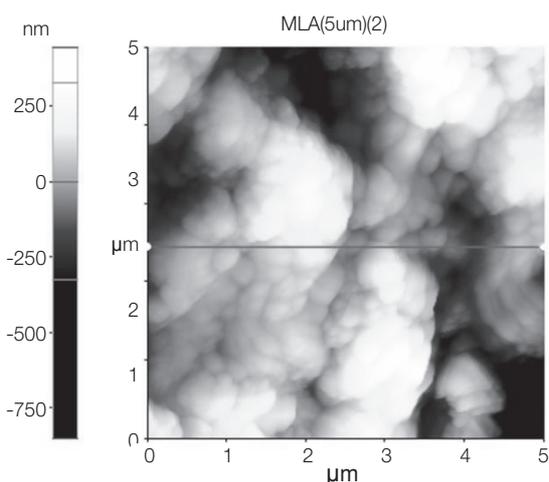


Figure 3. AFM image of single micro lens coated with porous silica particles.

However, MLA films coated with porous particles showed an increase in water CA, reaching $161.80 \pm 1.97^\circ$, as shown in inset Figure 2(d). Figure 2(a) shows the MLA sheet with $700 \mu\text{m} \times 700 \mu\text{m}$. Each particle had a $50 \mu\text{m}$ diameter and the gap between the particles was $8 \mu\text{m}$. Figure 2(b) shows the image of a porous particle ($1\text{--}3 \mu\text{m}$) coated on the MLA sheet. This figure clearly shows that the large hill of an MLA sheet is preserved in the superhydrophobic film after coating. Figure 2(c) is a larger image of the top of a single large particle. Therefore, our system that is consisted of large hemisphere micro pattern and relatively small porous particle imitated the lotus leaf structure well. It had micron-sized hills of MLA balls and nano-sized papilla of porous particles.

We used atomic force microscopy (AFM) to examine the surface roughness of superhydrophobic film in detail. We observed the smooth ball surface with a bare MLA sheet while we observed the rough surface on an MLA sheet incorporated with porous particles. The topographic image (Figure 3) shows

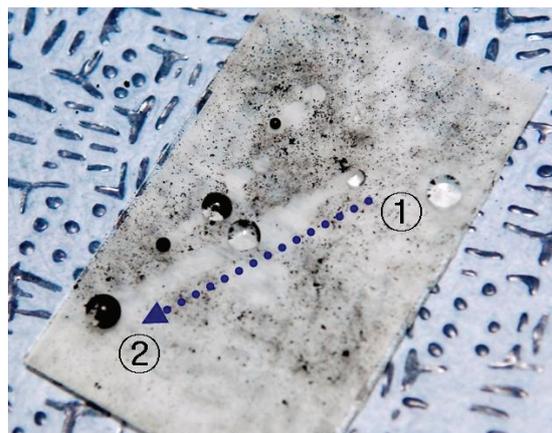


Figure 4. Demonstration of self-cleaning effect by rolling a water drop to remove the carbon black powder. An arrow shows the trace of a rolling water droplet.

a two level structure. As mentioned previously, we generated the dual-size hierarchical structure easily with a combination of large MLA balls and a small nanopapilla of porous particles. The quantitative analysis on the basis of the AFM images indicate that the root-mean-square roughness (R_q) is $492 \pm 48 \text{ nm}$ with porous particles on flat PET surface while the R_q is $900 \pm 14 \text{ nm}$ with porous particles on micro-patterned MLA sheet.

Wenzel¹⁷ and Cassie¹⁸ described the superhydrophobic phenomenon by the surface roughness of a hydrophobic surface and its hydrophobicity. Moreover, Ming *et al.* showed that the dual-size surface structure of the lotus leaf surface minimizes the contact angle hysteresis. Therefore the increased surface roughness factor to reach the Cassie regime requires rolling-off and bouncing of the droplets.¹¹

In our system, due to induced MLA pattern, the advancing and receding CA increased. The measured advancing was $157.50 \pm 1.70^\circ$ and receding CA was $154.31 \pm 1.20^\circ$. The CA hysteresis was about 3° . As a result of decrease of hysteresis of CA, sliding angle (SA) also dramatically decreased from 6 to $3 \pm 1^\circ$ and there are no pinned-on points in large area ($20 \text{ cm} \times 20 \text{ cm}$). (video clips clearly show this)

Therefore, surface roughness increased due to introduced MLA sheet and this change surpasses a critical level of Wenzel state and enters the Cassie state so that water droplets easily roll-off even an angle of as small as 3° .

To show the self-clean effect of the superhydrophobic film, we spread carbon black powders on the film surface. When several water droplets were sprayed on the surface, the contaminant was easily removed by simply rolling water drops off the surface. Figure 4 shows this self-cleaning effect on the superhydrophobic surface. The arrow in Figure 4 shows the swiped trace of the water drop that cleaned the contaminated surface. After a water drop (①) rolled on the contaminated surface, the carbon blacks were attached on the water surface (②).

In summary, we well imitated dual-sized structure of lotus leaf using porous particle and hemisphere MLA structure and this film showed a good superhydrophobic properties such as self-cleaning and rolling-water droplet at low sliding angle.

Experimental Section

Material. A large MLA sheet (120 cm × 120 cm) for the display device was kindly donated by LG Micron. The MLA sheet was prepared by the imprinting process with NOE 63. The silicon coating solution (I-2577) purchased from Dow Corning and used without further purification. The original coating solution consists of 60% dimethyl methylphenyl-methoxy siloxane, 30% toluene, and 10% methyltrimethoxy-silane. Aerosol silica particles (Micloid, ML381) were purchased from Dongyang Chemical, co. The advertised average particle size is about 1~5 μm and porosity of the particle was ~1.5 mL/g, as determined by the BET method.

Coating: Toluene 30 g was added into 70 g of original silicon solution to adjust viscosity of coating solution and then 1 g silica powder was poured into 9 g diluted coating solution. The final concentration of silica was 10 wt%. The mixed solution was thoroughly mixed with stirring for 24 hours.

Characterization. We used the SEO contact angle analyzer (Surface Electro Optics, Phoenix) to measure the static and dynamic contact angle. Static contact angles were measured by sessile drop method and reported values are averages of five measurements. Advancing and receding contact angles were recorded every 0.5 second for 10 second while the water was added to and withdrawn from the drop, respectively. The sliding angle measurement was performed with lab-made sliding angle measurement system. All angles were measured at ambient temperature. The surface topological measurements were performed under ambient conditions with AFM (XE-100 microscope, Park systems Corp.). We used the silicon cantilevers of a 910M-NCHR (non-contact mode, 42 N m⁻¹ force constant and 330 kHz resonant frequency) for morphology of surface.

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