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Fabrication of a Superhydrophobic Surface with Flower-Like Microstructures with a One-Step Immersion Process

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Superhydrophobicity of solid materials has attracted significant attention because it provides strong water repellency and self-cleaning properties.[1,2] The chemical composition and nano-/microscale structures of the surface are key factors determining the surface properties. Recently, superhydrophobic surfaces showing high water contact angles (CA) > 150º and low sliding angles (SA) < 10º have been the focus of much research because they have many applications in both academic fields and industrial processes.[3-5] The contact area between a water droplet and a superhydrophobic surface is minimized, and this phenomenon could have applications in fields such as anti-contamination,[6,7] anti-fogging,[8] anti-snow-sticking,[9] and antireflection.[10]

Superhydrophobic properties of solid surfaces are also used in nature. For example, lotus leaves have self-cleaning properties,[11] and the legs of a water strider allow it to stand on the surface of water.[12] Thus, many artificial superhydrophobic surfaces have been fabricated based on observations of these natural properties. Generally, the reported methods for fabricating superhydrophobic surfaces involve two-step procedures, harsh reaction conditions, and expensive instruments. As a result, there is a need for simple and inexpensive methods for fabricating superhydrophobic surfaces.

Two factors are required in the design of a superhydrophobic surface of a solid material: (1) a nano- and micro-rough structure on the surface, and (2) a coating made of a low-surface-energy material such as long fatty acids, alkyl thiols, or fluorinated alkyl silanes on the modified solid surface. Together, these factors provide a low-surface-energy hierarchical surface on the solid materials.[13-15] Various methods have been used to create hierarchical surfaces, such as electrochemical deposition,[16,17] lithography,[18,19] chemical etching,[20-22] electrospinning,[23,24] layer-by-layer deposition, chemical vapor deposition,[25] sol-gel methods,[26,27] and template methods.[28] A rough surface absolutely must be created to obtain a superhydrophobic surface, because the maximum water contact angle of a flat surface coated with low-surface-energy material is just 120º. Various fabrication methods have been reported, but very few are useful for commercialization. Therefore, it is necessary to develop a simple and easy procedure to fabricate superhydrophobic surfaces. In this study, we fabricate superhydrophobic surfaces with flower-like structures providing nano-/micro-roughness in a novel and facile one-step process by dipping Mg flakes into a solution of fluorinated alkyl silane and propylphosphonic acid in ethanol. The obtained rough surface morphology has flower-like shapes, and the degree of roughness can be controlled by tuning the dipping time.

Instrumentation. XPS analyses were performed using an XPS spectrometer (MultiLab 2000, Thermo VG Scientific). The morphologies of the samples were observed with a field-emission scanning electron microscope (FE-SEM, Hitachi S4300, Hitachi Inc.). The surface wettability was investigated by measuring the contact angle of a 5 μL water droplet on the sample surface using a contact angle analyzer (Phoenix 300, Surface Electro Optics) at room temperature. Before the fabrication, Mg plates with a size (1.0 cm × 1.0 cm × 0.1 cm) were cleaned ultrasonically for 20 min in ethanol. Heptadecafluoro-1,1,2,2-tetrahydrodecyl trimethoxysilane (HFTHTMS) was purchased from Gelest Inc. (U.S.A.). Propylphosphonic acid (95%) was purchased from Sigma-Aldrich. The different grades of ethanol were purchased from Duksan Chemical Co. (Korea, 95%, EP grade) and Samchun Chemical Co. (Korea, 99.5%, EP grade and 99.9% SP grade).

Experimental

Propylphosphonic acid (12.4 mg, 0.1 mmol) was added into a solution of HFTHTMS (80 mg, 0.14 mmol) in ethanol (Duksan Chemical Co., EP grade, 10 mL), stirred for 24 h at room temperature and then used as a coating solution. The Mg flake was cleaned in ethanol ultrasonically and then dried. The cleaned Mg flake was dipped into the coating solution for various time periods at room temperature. The coated Mg flakes were dried at room temperature and further used for the surface analysis.

Results and Discussion

The water contact angle on a clean Mg plate is 58º, meaning that the surface is very hydrophilic. However, the Mg surface became hydrophobic after the modification procedure. The procedure for fabricating a superhydrophobic surface on the Mg plate is simply to immerse the Mg plate into a coating solution for different time periods. This simple one-step preparation produces flower-like structures on the Mg surface (Figure 1). Figure 2 shows SEM images of the flower-like structures and water droplets on various Mg

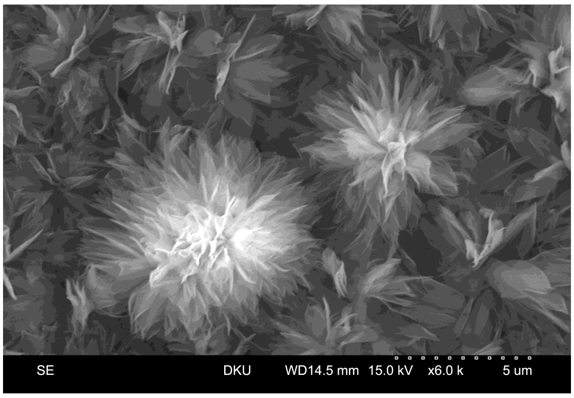

Figure 1. SEM image of flowerlike structures on an Mg plate coated with HFTHTMS and propylphosphonic acid in 95% ethanol.

plates obtained after different dipping periods. The images show flower-like structures of polysiloxane formed in the presence of propylphosphonic acid. To examine the role of propylphosphonic acid in the formation of the flower-like morphology, phosphoric acid was also used instead of propylphosphonic acid. In this case, the nano-/microscale hierarchical structure does not form on the Mg surface, the obtained surface has a low wettability (water contact angle = 115°), and the morphology was amorphous. Thus, it is confirmed that the propylphosphonic acid plays a key role affecting the flower-like morphology and acts as a crystal modifier.

We next examined the effect of different alkylphosphonic acids on the superhydrophobicity of the coated Mg surfaces. The superhydrophobicity of the modified Mg plate was monitored by measuring the water contact angle, and the morphology of modified Mg surface was observed using the SEM. The water contact angles on the samples obtained with different alkylphosphonic acids were not much changed, and as shown in Figure 3, the morphologies were also similar.

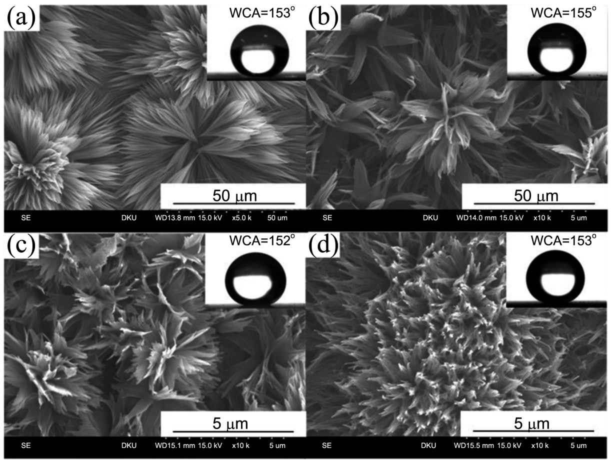

Figure 3. SEM images of Mg plates coated with a solution of HFTHTMS and different alkylphosphonic acids; (a) methylphosphonic acid, (b) propylphosphonic acid, (c) butylphosphonic acid, and (d) octylphosphonic acid.

We next applied the dip-coating procedure to various substrates for the fabrication of superhydrophobic surfaces under the same conditions. Figure 4 shows the water contact angle *versus* dipping time at room temperature for Mg, Cu, Al, and filter paper substrates. Mg and Cu showed stable superhydrophobic surfaces with high water contact angles (> 150°). However, Al sheet and filter paper show only moderate wettability.

As shown in Figure 5, the density of flower-like structures increased as the ethanol purity decreased for the same immersion period. The increased numbers of clusters and larger micro-scale roughness influenced the superhydrophobicity of the coated Mg surface. The petals obtained were uniform in size and had the least sharp tips.

The stability of these coated surfaces was evaluated by dipping the coated plates in water, dichloromethane, ethyl

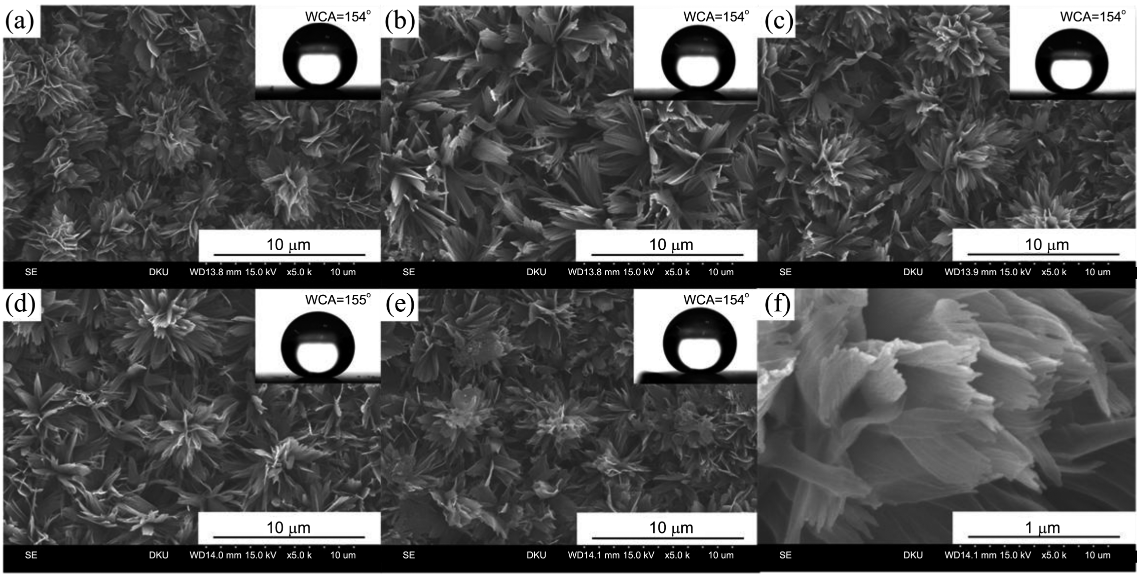

Figure 2. SEM images of the Mg surfaces obtained after immersion for (a) 1 h, (b) 6 h, (c) 12 h, (d) 18 h, and (e) 24 h and (f) high-magnification image of a sample obtained after 24 h of immersion.

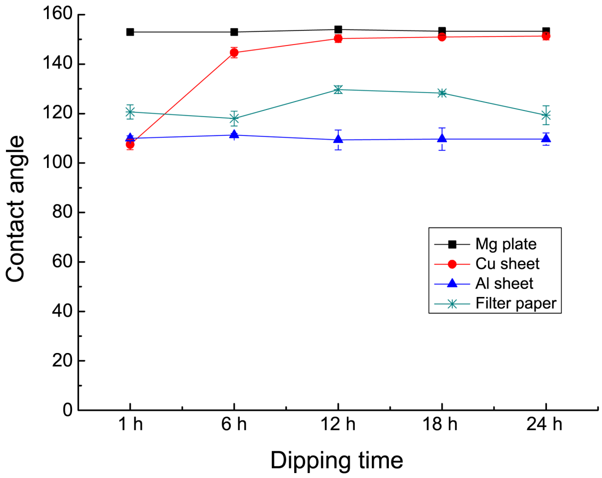

Figure 4. Water contact angles of various surfaces dipcoated with HFTHTMS and propylphosphonic acid in ethanol.

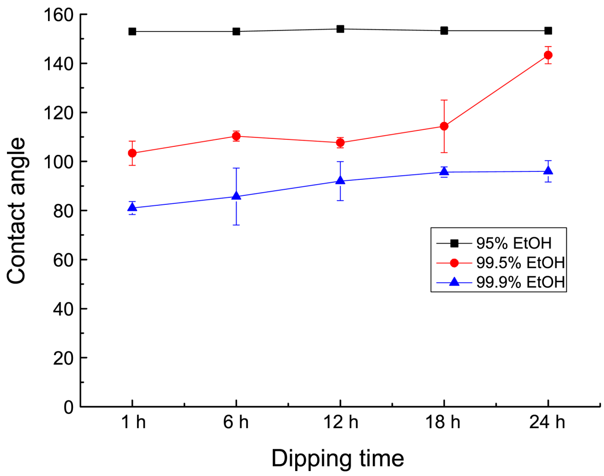

Figure 5. Relationship between the ethanol purity and the water contact angle.

acetate and ethanol for 6 h and then checking the water contact angle and morphology by SEM analysis. We found no change in the water contact angle and no deformation of the flower-like morphology of the Mg surface. These results confirm the stability of the coated surfaces on Mg plate in organic solvents and water.

The composition of the modified plate was confirmed by energy dispersive spectrometry (EDX) analysis. C, O, F, Mg, Si, and P peaks were observed in the EDX spectrum (the Al peak in the spectrum is due to the background). This result also confirms that the surface was completely coated with the coating materials (Figure 6).

Cassie and Baxter proposed that the roughness of a surface is an important factor for obtaining superhydrophobicity.[29] In the Cassie-Baxter model, the contact area between a water droplet and the surface of the plate should be minimized to obtain a superhydrophobic surface. For this purpose, the nano-/micro-rough structures on the surface hold air that prevents the water droplet from penetrating into the valleys of the rough structure on the solid surface. The following

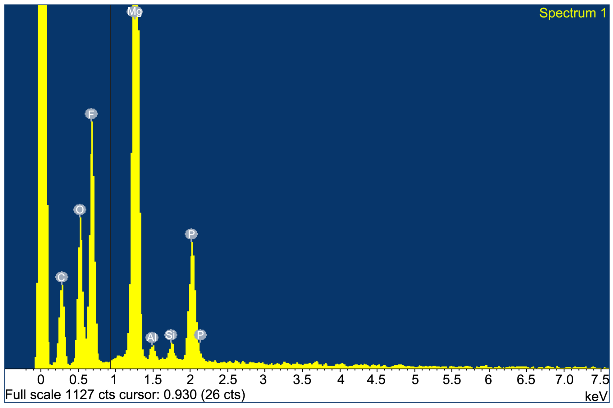

Figure 6. EDX spectrum of the modified Mg surface.

equation describes the relationship between the water contact angles of a modified rough surface and a flat solid surface. In our experiments, the flat surface is modified with HFTHTMS before the water contact angle is checked.

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

Here, θ is the water contact angle on the flat surface modified with HFTHTMS, θ^* is the water contact angle on the plate surface with the flower-like morphology, and Φ_s is the fraction of the base of the water droplet in contact with the solid plate. If the flower-like structures on the surface of the Mg plate contain a high volume of air, Φ_s becomes small. The water contact angles of the coated surfaces with the flower-like structures on Mg plate were $\theta^* = 154^o$, and the water contact angles of the flat Mg plate coated with HFTHTMS were 109^o. From the above equation, the Φ_s

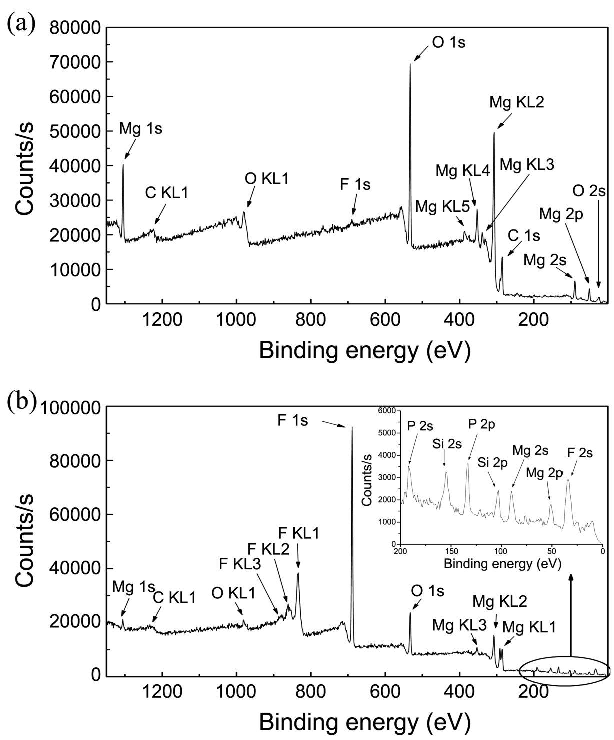

Figure 7. (a) XPS spectra of bare Mg. (b) XPS spectra of modified Mg plate.

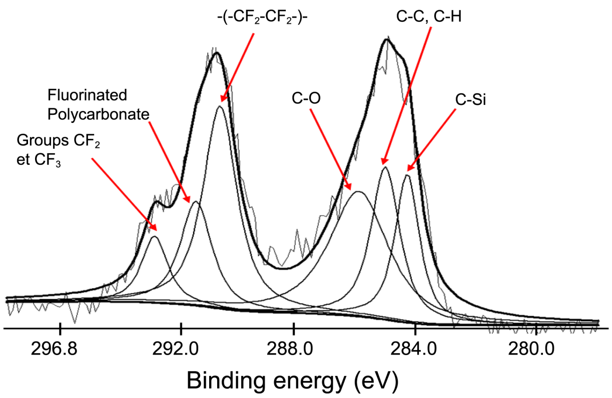

Figure 8. High-resolution C_{1s} XPS spectra of the modified hierarchical Mg surface.

value was calculated as 0.15. This confirms that only 15% of the water droplet is in contact with flower-like superhydrophobic surfaces of the coated Mg plate, and the rest of the water droplet is in contact with air. In this situation, the contact between the water droplet and the modified surface is fairly small, so the water droplet moves very easily at a small tilt angle.

The surface chemical composition was characterized by X-ray photoelectron spectroscopy (XPS). The spectra show that the modified surface of the Mg plate is composed of Si, F, O, and C (Figure 7). The highest peak at 688 eV is attributed to the C-F groups in HFTHTMS. The three peaks located at 190, 133, and 102 eV correspond to P_{2s}, P_{2p}, and Si_{2p}. In the high-resolution C_{1s} XPS spectra, C-Si, C-C, and C-O groups are found at 284.2, 285, and 285.9 eV and CF_2-CF_2, fluorinated polycarbonate, and -CF_2- are found at 290.5, 291.4, and 292.8, respectively (Figure 8). It can thus be concluded that the surface of Mg plate is coated with fluorinated silanes and propylphosphonic acids.

In summary, it has been demonstrated that flower-like microstructures can be fabricated on a Mg plate using a solution of propylphosphonic acid and HFTHTMS in ethanol. In the presence of propylphosphonic acid, the HFTHTMS is polymerized and then deposited on the surface of the Mg plates during the immersion period. Many flower-like structures were formed on the surface after at least 6 h of immersion, at which point the modified plate became superhydrophobic. The nano-/micro scale flower-like structure is composed of fluorinated polysiloxane, which acts as a low-surface-energy material. SEM images reveal that the flower-like structure is composed of many thin flakes. It is confirmed that these structures on the surface contain air and result in an ideal structure for obtaining the superhydrophobic surface. This proposed coating method is simple and can be applied to a large sample to fabricate a superhydrophobic surface without expensive instruments.

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