Fabrication of Superhydrophobic Conical Structures of Polysiloxane on Mg Plates Using an Immersion Process

Seungcheol Go, Younga Kim, and Yonghyun Ahn*

*Department of Chemistry, GRRC, Dankook University, Yongin 448-701, Korea. *E-mail: yhahn@dankook.ac.kr*

Superhydrophobic surfaces have drawn the attention of the scientific and industrial communities alike owing to their immense potential to contribute to fundamental research and practical applications.[1-4] Superhydrophobic surfaces can be used in self-cleaning,[5] ice resistance,[6] and applications in nano-/micro-fluidic devices.[7] Many biological surfaces such as the lotus leaf, and the legs of a water spider are water repellent. Notably, the structure and chemical properties of a surface are the key factors that determine the superhydrophobicity of the surface of a material. For instance, the numerous papillae on the lotus leaf are coated with wax, which is a low surface energy material. The papillae on the lotus leaf and the conical structures on legs of the water spider[8] are crucial in lending superhydrophobic properties to the surfaces. Nano-/micro-binary structures on surfaces trap air and dramatically reduce the contact area between the surface and the water droplet. Superhydrophobic surfaces have been conventionally fabricated by creating nano-scale hierarchical structures and by coating the surfaces with materials of low-surface-energies. Fluorinated alkyl silanes and long chain fatty acids are commonly used as low-surface-energy materials. However, Cassie-Baxter's model demonstrated that rough surface structures are important to retain air, as they cushion water droplets.[9] Provided that a large amount of air is retained on the surface, the surface can be expected to show superhydrophobic properties. Therefore, an appropriate conformation and morphology of the surface are crucial factors to realize superhydrophobic surface properties.

Many techniques including etching,[10-12] sol-gel methods,[13-15] phase-separation methods,[16,17] electro chemical deposition,[18,19] electrospinning,[20,21] and lithography[23] have been used to create rough surfaces. Conical nano-/micro-binary structures on the surface have received considerable attention because of their geometry and physical properties. Conical surface structures have been fabricated using a variety of materials. For instance, conical nanocarbon structures have been fabricated on a transparent and flexible substrate using an ion irradiation technique at low temperatures.[24] These structures were found to exhibit superior field emission properties as compared to carbon nanotubes. In another example, nickel surfaces containing nano-/micro conical arrays were produced by electrodeposition in the presence of ethylenediamine.[25-27] The modified nickel surfaces exhibited super-

hydrophobicity without requiring modification with low surface energy materials. Further nanoconical arrays of glass have also been obtained using a chemical etching process.[28]

Even though nanoconical structures have gained considerable focus for various applications ranging from electronic devices to the fabrication of superhydrophobic surfaces, materials that can be used for assembling nanoconical structures are limited. In the present work, we report a simple method to fabricate superhydrophobic surfaces containing nanoconical structures on Mg plates using fluorinated alkyl triethoxysilane and 1,6-diphosphonohexane. This one-step process is simple and can be applied to large surfaces.

Experimental Section

Instrumentation and Materials. A field-emission scanning electron microscope (FE-SEM, Hitachi S4300, Hitachi Inc.) was used for assessing the morphology of the surfaces. Analysis of the surfaces by X-ray photon electron spectroscopy (XPS) was carried out using a spectrometer (MultiLab 2000, Thermo VG Scientific).

Heptadecafluoro-1,1,2,2-tetrahydrodecyl trimethoxysilane (HFTHTMS) was purchased from Gelest Inc. (U.S.A). Synthesis of 1,6-diphosphonohexane was carried out according the method previously reported.[29] Mg plates with dimensions 1.0 cm × 1.0 cm × 0.12 cm were cleaned ultra-sonically with 5% HCl for 2 min and subsequently washed with distilled water and ethanol, after which they were used for the experiments.

Procedure. To a solution of HFTHTMS (0.08 g, 0.14 mmol) in ethanol (10 mL), 1,6-diphosphonohexane (0.043 g, 0.1 mmol) was added. After continuous stirring for 24 h at room temperature, the ultra-sonically cleaned Mg flake was dipped in this solution for various time periods at room temperature. The coated Mg samples were dried at 80 °C in an oven and then cooled to room temperature.

Results and Discussion

We evaluated the surface morphologies of the coated samples by FE-SEM. The SEM images in Figure 1 show the structures on the surface of an Mg plate that was (a) uncoated, (b) coated with HFTHTMS, (c) coated with 1,6-diphosphonohexane, and (d) coated with a solution of
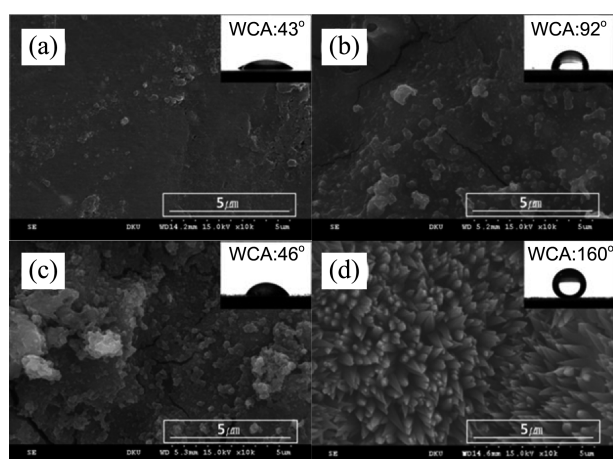
Figure 1. (a) Uncoated Mg-plate; Mg plate coated with (b) HFTHTMS; (c) 1,6-phosphonohexane; (d) a solution containing a mixture of HFTHTMS and 1,6-diphosphonohexane in ethanol.

Figure 3. The relationship between the contact angle of water on coated Mg surfaces and the concentration of 1,6-diphosphono-hexane.

HFTHTMS and 1,6-diphosphonohexane. It is noted that HFTHTMS which is a low surface energy material, cannot alone be expected to improve the superhydrophobicity of the Mg surface. Figure 2 shows the SEM images of the coated surface of the Mg plate after immersion in a solution of 1,6-diphosphonohexane and HFTHTMS in ethanol for (a) 6, (b) 7, (c) 12, and (d) 24 h. As shown by the figure, the morphology of the surface of the Mg plate depends on the immersion period.

At an early stage, polysiloxanes were deposited on the surface of the Mg plate in the form of amorphous particles, while after 6 h, nanocones formed as islands. The nanocone clusters expanded, depending on the immersion period, and finally fused after 24 h of immersion. The period of immersion affected the formation of nano-/micro-conical structures and controlled the growth of the cones. In the absence of 1,6-diphosphonohexane, neither nanorods nor nanocones formed on the surface of Mg.

We examined the effect of different concentrations of 1,6-diphosphonohexane on the wettability of the coated Mg surfaces. The wettability of the coated Mg plate was monitor-
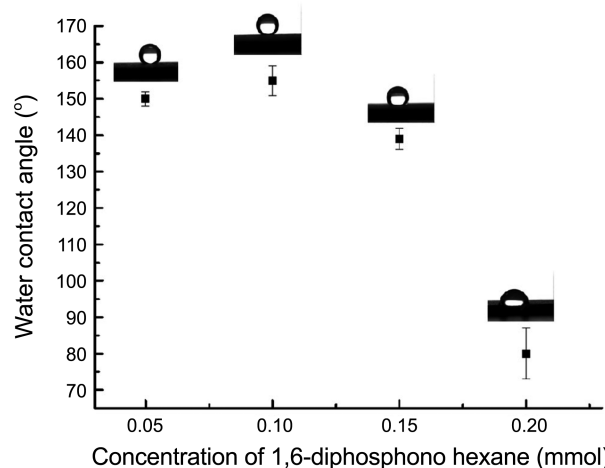
ed by measuring the contact angle of water. As shown in Figure 3, the contact angle of water on the samples obtained with different concentrations of 1,6-diphosphonohexane varied. The highest water contact angle was obtained at 0.1 mmol of 1,6-diphosphonohexane. As the concentration of 1,6-diphosphonohexane increased from 0.05 mmol to 0.2 mmol, the contact angle of water decreased from 155° to 90°. These results could be ascribed to the increase in the amount of the phosphate group on the coated surface and the formation of amorphous structures on the surface.

XPS was carried out to confirm the presence of phosphate groups on the coated surface of the Mg plate. Figure 4 shows that the modified Mg surface contained F, O, C, Si, and P. The strong peak originating from F at 689.3 eV was observed from the surface of the modified Mg plate. The peak at 132.6 eV confirmed the presence of phosphorous (P_{2p}). The high resolution of C_{1s} peak is shown in Figure 5. The peaks originating from CF_2 (or CF_3) and C-C groups from the modified Mg surface were observed at 291.3 and 284.8 eV, respectively. The peaks corresponding to C-O (at 285.9 eV) and C-Si (at 284.2 eV) were also observed in the XPS
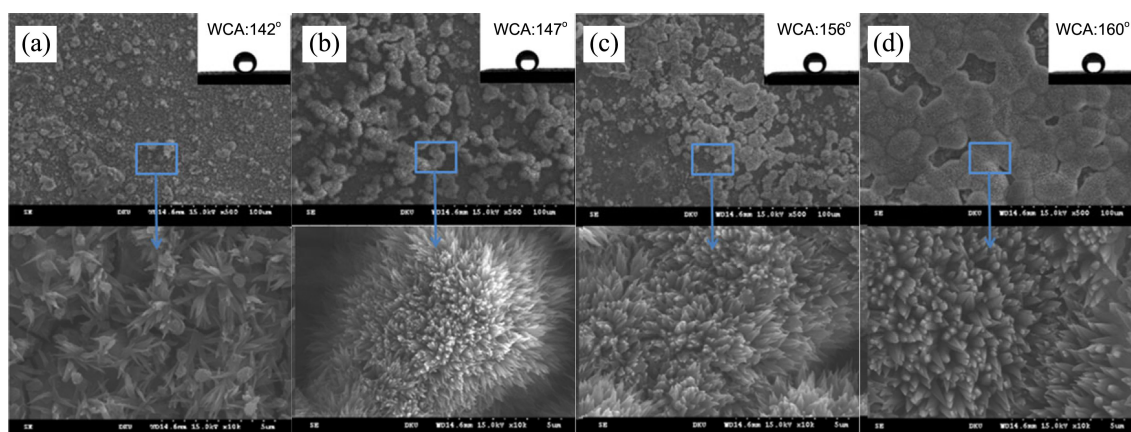

Figure 2. SEM images and water droplets on the surface obtaining by immersing the Mg plates in a mixture of HFTHTMS and 1,6-diphosphonohexane in ethanol for (a) 6 h, (b) 7 h, (c) 12 h, (d) 24 h.
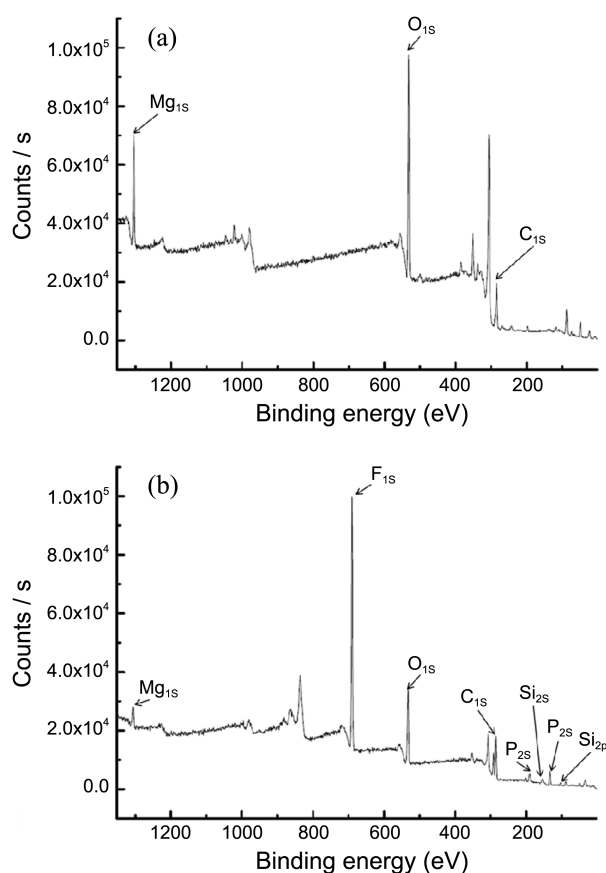
Figure 4. Spectra obtained by subjecting the (a) uncoated Mg-plate. (b) Mg-plate coated with a solution of HFTHTMS and 1,6-diphosphonohexane in Ethanol to XPS.

Figure 5. High-resolution spectra of C_{1S} and O_{1S} obtained by subjecting the coated Mg plate to XPS analysis.

spectrum. Quantitative analysis of the chemical composition of the surface also clearly confirmed the functionalization of the Mg surfaces with the fluorinated alkyl silane. The fluorine content on the surface of the Mg plate was 36.3%, indicating that the modified surface contained a sufficient amount of fluorine and the large amounts of fluorocarbon, which contributed to the superhydrophobicity of the surface.

The Cassie-Baxter equation shows the relationship between the wettability of a plane surface and a rough surface.

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

In this equation, θ represents the contact angle of water on the plane surface and θ^* represents the contact angle of water on the coated rough surface. Φ_s is the ratio of the area of the surface in contact with the water droplet to that in contact with air. The equation shows the superhydrophobicity of the modified rough surfaces that consist of the spaces between cones. The spaces can trap air, which prevents the penetration of water into the space. The air trapped in a rough surface acts as a cushion for water droplets and reduces the area of contact between a water droplet and the modified rough surface. The significantly low value of Φ_s in such a case indicates the significant extent of superhydrophobicity of the hierarchical nano-/micro-conical surfaces. The value of Φ_s of the conical structures formed on the Mg plate
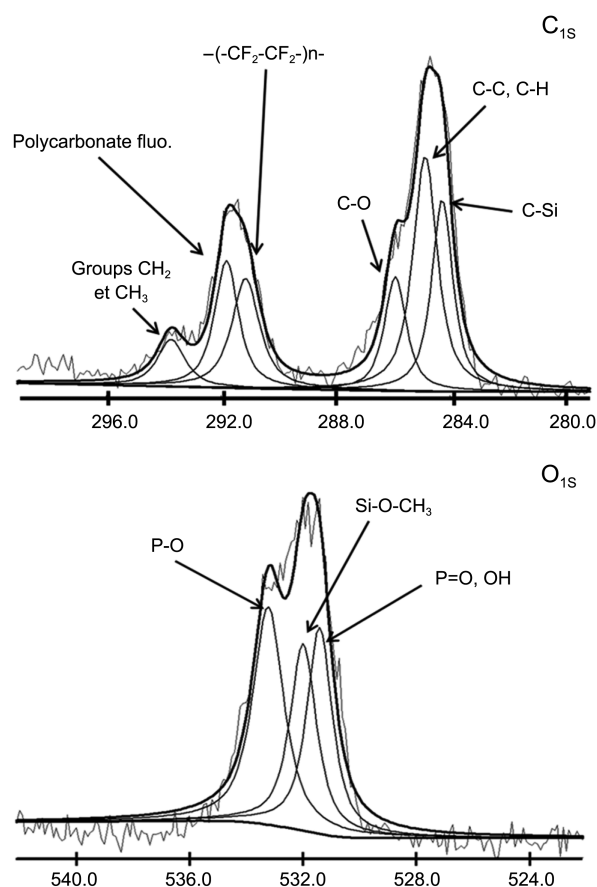
obtained by using the contact angles of water of the untreated ($\theta = 92^o$) and modified Mg plate ($\theta^* = 160°$) was 0.0625. The lower value of Φ_s indicated that the modified hierarchical surface retained a large volume of air. Further, 93.7% of the contact area between the nanoconical surface of the Mg plate and the water droplet was found to be composed of air. The resulting superhydrophobic surface showed the absence of wetting with water. Water droplets that fell on the modified surface completely bounced and rolled off the surface, which is also observed in the case of water droplets that fall on a lotus leaf (Figure 6).

As mentioned before, the composite mixture of fluorinated alkyl triethoxysilane and 1,6-diphosphonohexane created a nanoconical structure on the Mg surface. In addition to
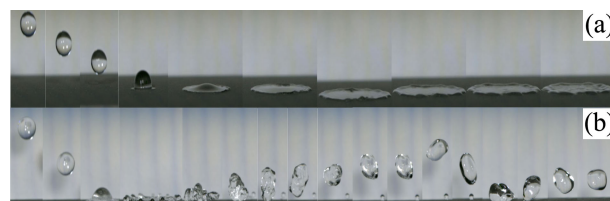

Figure 6. Dynamic interactions of water droplets with the surface of the (a) uncoated Mg-plate and (b) Mg-plate coated with a solution of HFTHTMS and 1,6-diphosphonohexane in ethanol, captured using a high-speed camera (at a speed of 5000 pictures per second).

retaining large amounts of air, the surface also exhibited a low surface energy. The superhydrophobicity of the modified surface was only observed after the formation of the nanoconical structures on the Mg plate. Since the wettability of the modified surface depended on both the chemical composition and the geometrical structures present on the surface, the presence of nanoconical structures on the surface provided an ideal conformation to achieve superhydrophobic surface properties without the need for coating the surface with a material of low surface energy. In our study, the presence of the high fluorine content, in addition to the nanoconical surface structure, increased the superhydrophobicity.

In conclusion, a superhydrophobic conical surface could be fabricated on Mg plates by a single-step technique involving immersion into a solution of a mixture of fluorinated alkyl triethoxysilane and 1,6-diphosphonohexane in ethanol at room temperature. The contact angle of water on the Mg surface containing the conical structures was 160°. The formation of the nanoconical structures depended on the immersion period and the presence and concentration of 1,6-diphosphonohexane, which acted as a structural modifier. This study validates our single-step method of fabricating superhydrophobic surfaces on solid materials, which is better than the traditional two-step methodology. The method we have proposed may be valuable for the efficient manufacturing of large-area superhydrophobic surface.

References

1. Guo, Z.; Liu, W.; Su, B. L. *J. Colloid. Interface. Sci.* **2011**, *353*, 335.
2. Xue, C. H.; Jia, S. T.; Zhang, J.; Ma, J. Z. *Sci. Technol. Adv. Mater.* **2010**, *11*, 033002.
3. Bhushan, B.; Jung, Y. C. *Progress Materials Sci.* **2011**, *56*, 1.
4. Shirtcliffe, N. J.; McHale, G.; Newton, M. I. *J. Polym. Sci. B: Polym. Phys.* **2011**, *49*, 1203.
5. Sethi, S.; Ge, L.; Ci, L.; Ajayan, P. M.; Dhinojwala, A. *Nano Lett.* **2008**, *8*, 822.
6. Menini, R.; Ghalmi, Z.; Farzaneh, M. *Cold Reg. Sci. Technol.* **2011**, *65*, 65.
7. Gau, H.; Herminghaus, S.; Lenz, P.; Lipowsky, R. *Science* **1999**, *283*, 46.
8. Gao, X. F.; Jiang, L. *Nature* **2004**, *432*, 36.
9. Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.
10. Park, K. C.; Choi, H.; Chang, C. H.; Cohen, R. E.; McKinley, G. H.; Barbastathis, G. *ACS Nano* **2012**, *6*, 3789.
11. Wang, Y.; Lu, N.; Xu, H.; Shi, G.; Xu, M.; Lin, X.; Li, H.; Wang, W.; Qi, D.; Lu, Y.; Chi, L. *Nano Res* **2010**, *3*, 520.
12. Han, M.; Go, S.; Ahn, Y. *Bull. Kor. Chem. Soc.* **2012**, *33*, 1363.
13. Lakshmi, R. V.; Bharathidasan, T.; Basu, B. J. *Appl. Surf. Sci.* **2011**, *257*, 10421.
14. Basu, B. J.; Hariprakash, V.; Aruna, S. T.; Lakshmi, R. V.; Manasa, J.; Shruthi, B. S.; *J. Sol-Gel Sci. Technol.* **2010**, *56*, 278.
15. Li, D.; Huang, F.; Ding, S. *Appl. Surf. Sci.* **2011**, *257*, 9752.
16. Brown, P. S.; Talbot, E. L.; Wood, T. J.; Bain, C. D.; Badyal, J. P. S. *Langmuir* **2012**, *28*, 13712.
17. Go, S.; Han, M.; Ahn, Y. *Bull. Kor. Chem. Soc.* **2012**, *33*, 3899.
18. Sarkar, D. K.; Paynter, R. W. *J. Adhesion Sci. Technol.* **2010**, *24*, 1181.
19. Zhang, X.; Shi, F.; Yu, X.; Liu, H.; Fu, Y.; Wang, Z.; Jiang, L.; Li, X. *J. Am. Chem. Soc.* **2004**, *126*, 3064.
20. Asmatulu, R.; Ceylan, M.; Nuraje, N. *Langmuir* **2011**, *27*, 504.
21. Singh, A.; Steely, L.; Allock, H. R. *Langmuir* **2005**, *21*, 11604.
22. Li, Y.; Zhang, J.; Zhu, S.; Dong, H.; Jia, F.; Wang, Z.; Tang, Y.; Zhang, L.; Zhang, S.; Yang, B. *Langmuir* **2010**, *26*, 9842.
23. Shiu, J. Y.; Kuo, C. W.; Chen, P.; Mou, C. Y. *Chem. Mater.* **2004**, *16*, 561.
24. Ghosh, P.; Yusop, M. Z.; Satoh, S.; Subramanian, M.; Hayashi, A.; Hayashi, Y.; Tanemura, M. *J. Am. Chem. Soc.* **2010**, *132*, 4034.
25. Hang, T.; Hu, A.; Ling, H.; Li, M.; Mao, D. *Appl. Surf. Sci.* **2010**, *256*, 2400.
26. Hang, T.; Li, M.; Fei, Q.; Mao, D. *Nanotechnology* **2008**, *19*, 035201.
27. Tian, F.; Hu, A.; Li, M.; Mao, D. *Appl. Surf. Sci.* **2012**, *258*, 3643.
28. D'Urso, B.; Simpson, J. T.; Kalyanaraman, M. *J. Micromech. Microeng.* **2007**, *17*, 717.
29. Ackerman, B.; Jordan, T. A.; Eddy, C. R.; Swern, D. *J. Am. Chem. Soc.* **1956**, *78*, 4444.