

Fabrication of a Superhydrophobic Triphenylene Ether Derivative Film on an Al Plate

Jisu Hwang, Younga Kim, and Yonghyun Ahn*

Department of Chemistry, GRRC, Dankook University, Yongin 448-701, Korea. *E-mail: yhahn@dankook.ac.kr
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In recent years, superhydrophobic surfaces have received much attention owing to their smart functions such as self-cleaning property, water repellent property, anticontamination, and anti-icing.¹⁻³ In nature, many plants, animals, and insects exhibit superhydrophobicity, and this phenomenon motivates researchers to fabricate new superhydrophobic surfaces for practical applications.

The most famous example of such a surface is the lotus leaf surface, which is composed of a nano/microscale rough structure and covered with a low-surface-energy material (*i.e.*, wax).⁴ The self-cleaning property of lotus leaf can be attributed to superhydrophobicity. A superhydrophobic surface has a high water contact angle ($> 150^\circ$) and a low sliding angle ($< 10^\circ$). The nano/microscale rough structure minimizes the contact between a particle and the surface of lotus leaf. Thus, the contamination on lotus leaf can be easily removed with water droplets. Therefore, the surface of lotus leaf is always maintained clean. These results have shown that the surface wettability of biological systems can be attributed to the nano/microscale roughness of the surface and the properties of surface-coated materials. Based on these observations, many efforts have been devoted to fabricate artificial biomimetic surfaces with various materials. In general, a superhydrophobic surface is fabricated in two steps: (1) creation of nano/microscale roughness and (2) chemical treatment of the rough surface with a low-surface-energy material. The created rough nano/microstructures on the surface trap air between them, and the trapped air prevents the penetration of water.

Various fabrication methods for nano/microscale hierarchical rough surfaces have been reported by mimicking natural surfaces, such as chemical etching,⁵⁻⁷ sol-gel,⁸⁻¹¹ lithography,¹²⁻¹⁵ spray,¹⁶⁻¹⁹ and self-assembly coating.²⁰⁻²³

To fabricate superhydrophobic metal surfaces, nano/microscale rough surfaces should be treated with low-surface-energy materials because clean metal surfaces are usually hydrophilic. Although numerous methods have been reported for the fabrication of hierarchical surfaces, low-surface-energy materials used for coating metal surfaces are limited. Fluorinated long alkylthiols^{24,25} or long alkyl carboxylic acids²⁶⁻²⁸ and fluorinated alkylsilanes^{29,30} have been used as the low-surface-energy materials to modify hydrophilic metal surfaces by reacting with the surface hydroxyl groups to afford the corresponding superhydrophobic surfaces.

In this paper, we report the fabrication of a superhydro-

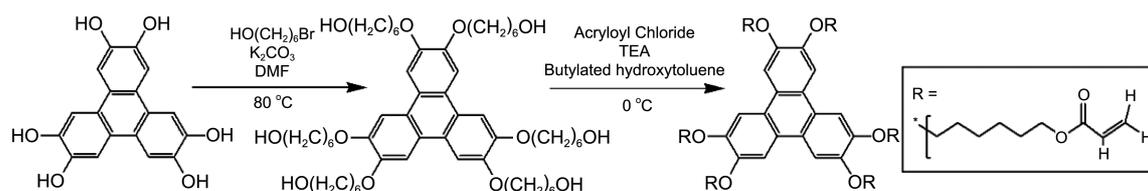
phobic surface on Al alloy. The nano/microscale roughness of Al surface was created by chemical etching, and the surface energy was lowered by the UV curing of the Al plate with 2,3,6,7,10,11-hexakis(6-acryloyloxyhexyloxy)triphenylene (HAHTP). The acryloyl group of HAHTP induced photopolymerization. The effects of HAHTP concentration and immersion period on the superhydrophobicity of Al surface were evaluated. The superhydrophobic surface of modified Al plate was analyzed by scanning electron microscopy (SEM), energy dispersive spectrometry (EDX), and water contact angle. HAHTP was prepared using a reported literature procedure.³¹

Experimental

Materials.

2,3,6,7,10,11-Hexakis(6-hydroxyhexyloxy)triphenylene (1): 2,3,6,7,10,11-Hexahydroxytriphenylene hydrate (1 g, 3.0 mmol) and K_2CO_3 (8.5 g, 61.6 mmol) were added to a flask containing dimethylformamide (DMF, 100 mL) and heated at 80 °C. A solution of 6-bromo-1-hexanol (5.5 g, 30.8 mmol) in DMF (20 mL) was added dropwise to the reaction mixture, and the resulting mixture was refluxed for 20 h. Then, the reaction mixture was cooled to room temperature, and ethyl acetate (100 mL) was added and stirred for 30 min. Brine (20 mL) was added, and the organic layer was separated twice. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by silica column chromatography. (CH_2Cl_2 :MeOH = 13:2) Yield: 2.18 g (78.5%). ¹H NMR (200 MHz, $CDCl_3$) δ 1.45-1.73 (m, 36H), 1.86-2.06 (m, 12H), 3.68 (t, $J = 6.4$ Hz, 12H), 4.24 (t, $J = 6.2$ Hz, 12H), 7.82 (s, 6H).

2,3,6,7,10,11-Hexakis(6-acryloyloxyhexyloxy)triphenylene (HAHTP) (2): Triethylamine (TEA, 6.6 mL, 47 mmol) was added to a solution of **1** (2.18 g, 2.35 mmol) in a mixture of CH_2Cl_2 (90 mL) and tetrahydrofuran (THF, 10 mL), and the resulting mixture was stirred at 0 °C for 30 min in Ar atmosphere. Acryloyl chloride (2.86 mL, 35 mmol) and butylated hydroxytoluene (0.15 g, 0.75 mmol) were dissolved in CH_2Cl_2 (50 mL), the resulting solution was stirred at room temperature for 5 min, and then added dropwise into the mixture of **1** for 20 min. The reaction mixture was stirred at 0 °C for 4 h in argon atmosphere. After removing the TEA salt by filtration, the filtrate was evaporated. The residue was



Scheme 1. Preparation of HAHTP.

dissolved in CH_2Cl_2 (50 mL) and successively washed with aqueous NaHCO_3 , and brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The crude product was recrystallized from ethanol at low temperature. Yield 1.7 g (59%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.43-1.78 (m, 36H), 1.89-1.99 (m, 12H), 4.15-4.26 (m, 24H), 5.79 (d, $J = 10.8$ Hz, 6H), 6.10 (dd, $J = 17.6$ Hz, 10.4 Hz, 6H), 6.38 (d, $J = 17.6$ Hz, 6H), 7.82 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.4, 148.9, 130.6, 128.6, 123.7, 107.4, 69.5, 64.5, 29.4, 28.6, 25.8, 25.7; FT-IR (cm^{-1}): 2929, 1720, 1638, 1600-1400, 985, 905.

Fabrication Procedure for Al Plate. Al plate (FCK 42) was purchased from K&S (U.S.A). The commercial Al plates were cut into pieces (20 mm \times 20 mm \times 0.2 mm). The Al plates were successively washed with ethanol and di-

stilled water for 5 min. Then, the dry Al plates were immersed in 3 N HCl for 20 min. After the corroding, the plates were washed ultrasonically with distilled water for 10 min and dried at 40 °C overnight. The clean etched Al plates were immersed in beaker containing a solution of 0.62 g of **2** and 0.06 g of Runtecure1108 as the initiator in 5 mL CH_2Cl_2 . After 10 min, the Al plates were dried at room temperature and cured under UV radiation (365 nm) for 10 min.

Results and Discussion

Al is a hydrophilic material, and its surface is covered with an oxide layer. The unmodified Al plate is smooth, and the water contact angle of the unetched Al plate is 109°. Because of the relative hydrophilicity of Al alloy, the coating of a

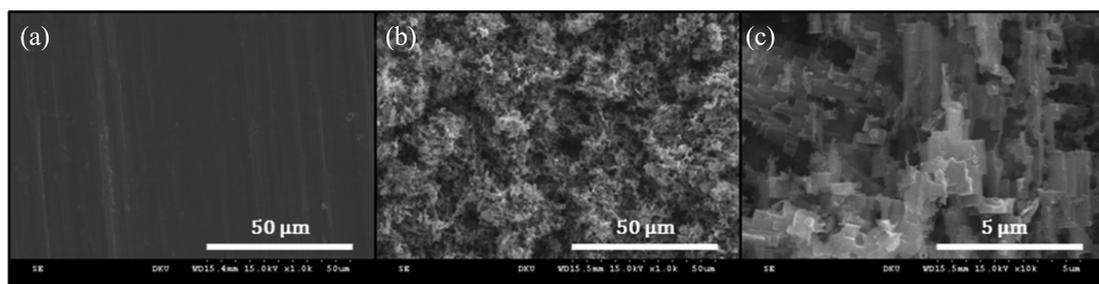


Figure 1. Scanning electron microscopy images of the Al plate surface (a) before and (b) after chemical etching, (c) magnification of (b).

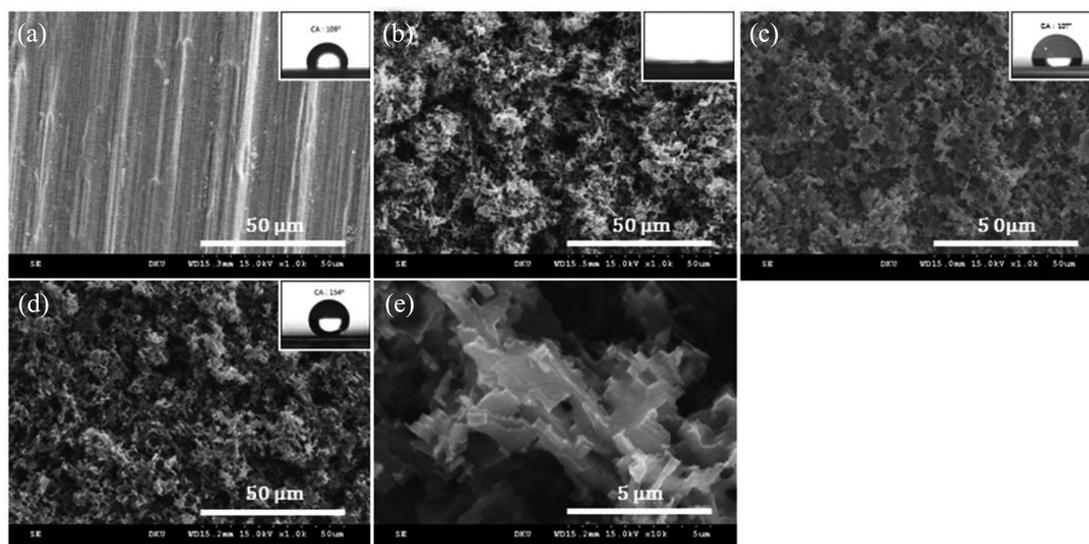


Figure 2. Scanning electron microscopy images of the Al plates: (a) untreated, (b) treated with 3 N HCl, (c) coated with 2,3,6,7,10,11-hexakis(6-acryloyloxyhexyloxy)triphenylene (HAHTP) monomer, (d) modified with HAHTP polymer, and (e) magnification of (d). The insets are the photographs of 5 μL water droplet.

low-surface-energy material is necessary to obtain a superhydrophobic surface on Al alloy. A photopolymerizable triphenylene compound, HAHTP, was synthesized (Scheme 1) and used to fabricate the superhydrophobic surface of the etched Al plate.

The surface morphology of the Al plate was characterized by SEM. The surface morphology of the modified Al plate is shown in Figure 1. The untreated surface of the Al plate is smooth. After, the Al plates were treated with an HCl solution, many holes were formed on the Al plate surface. The high-resolution SEM images of the etched Al plate surface show irregular protuberances and holes (Figure 1(c)).

Figure 2 shows the SEM images of the Al plates (a) unetched, (b) treated with 3 N HCl, (c) coated with HAHTP monomer, and (d) modified with HAHTP polymer. After the etching with a 3N HCl solution, the surface of the Al plate became superhydrophilic and the water contact angle of the etched Al plates could not be measured (Figure 2(b)). The etched Al plates were modified with an HAHTP solution to fabricate a superhydrophobic surface. Before the UV curing, the Al plate coated with the monomer, HAHTP, showed a low water contact angle (107° , Figure 2(c)). After the polymerization of HAHTP, the modified Al plate showed superhydrophobicity with a water contact angle of 154° . In addition to high wettability, there was no obvious change in the nano/microscale roughness and conformation after the UV curing of HAHTP. This nano/microstructure on the modified surface traps air between the structures, and the trapped air prevents the penetration of water into the holes. The nano/microstructure and a low-surface-energy material are the key to obtain a superhydrophobic surface.

To establish the variation in the water contact angles with the HAHTP concentration, a series of experiments were conducted under different HAHTP concentrations. The water contact angles of the modified etched Al plate with different HAHTP concentrations are shown in Figure 3. When 0.1 mol of HAHTP was used, the water contact angle is greater than 150° . The wettability of modified Al plate decreased

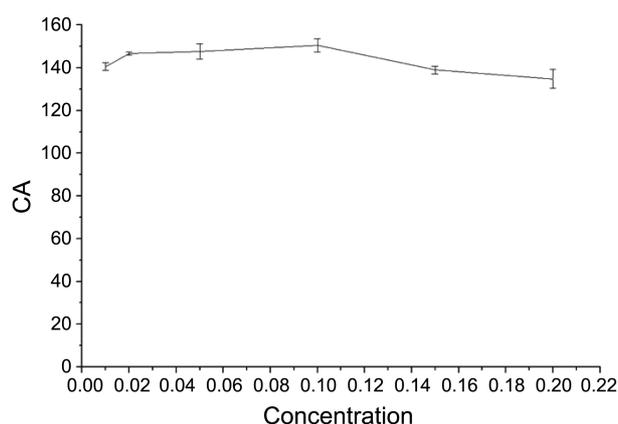


Figure 3. Relationship between different concentrations of HAHTP and water contact angle on superhydrophobic surfaces.

when the HAHTP concentration in the coating solution increased to > 0.1 moles of HAHTP. Clearly, the optimum water contact angle was obtained below < 0.1 mol of HAHTP. Thus, the hydrophobicity of modified Al plates depends on the concentration of HAHTP.

The chemical compositions of the chemically etched and modified Al plates after UV curing of HAHTP were analyzed and compared by X-ray photoelectron spectroscopy (XPS). The XPS spectrum of the modified Al plate shows that the C_{1s} peak increased (Figure 4(a)). The C/O ratio increased from 0.16 to 1.17 after the coating with HAHTP. The high-resolution analysis of C_{1s} peak shows three peaks at 284.6 eV (C-C, and C-H), 286.5 eV (C=C), and 288.9 eV (COOR). These results confirmed that the modified Al plate is coated with a polymer of HAHTP. The surface chemical composition of the Al plates was characterized by the EDX spectrum. The C, O, and Al peaks were observed in the EDX spectrum. The presence of a C peak confirms that the modified surface was completely coated with a polymer of HAHTP (Figure 5).

The Cassie–Baxter equation shows that the surface charac-

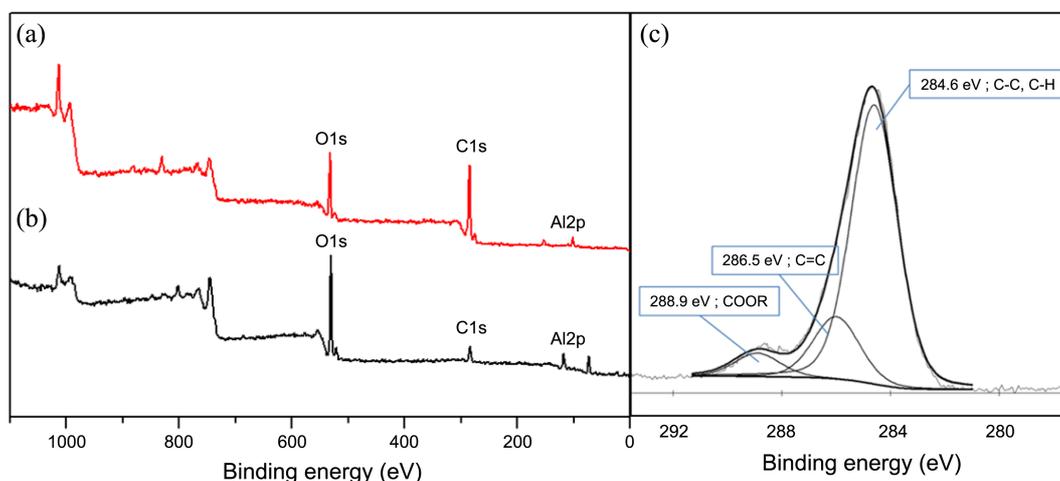


Figure 4. X-ray photoelectron spectroscopy spectra of (a) Al plate modified with 2,3,6,7,10,11-hexakis(6-acryloyloxyhexyloxy)triphenylene (HAHTP) polymer after etching the Al plate, (b) chemically etched Al plate, and (c) high-resolution C_{1s} spectra of the Al plates chemically etched and modified with HAHTP polymer.

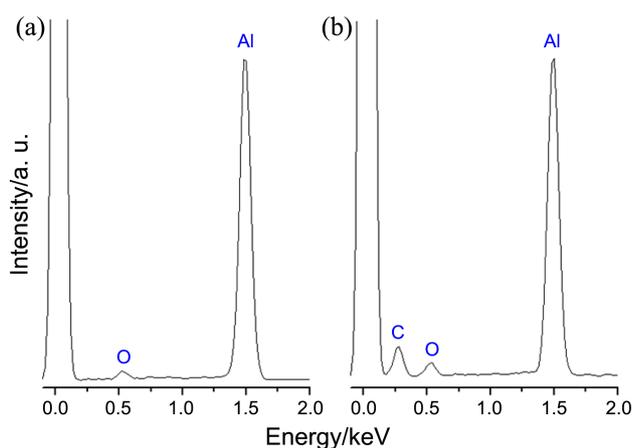


Figure 5. Energy dispersive spectrometry spectra of (a) etched and (b) polymer-coated Al plate after etching.

teristic is a key factor to determine the superhydrophobicity of a surface. The contact area between the modified Al plate and a water droplet should be minimized to obtain a superhydrophobic Al plate. The relationship between the water contact angle of a coated flat Al plate surface and coated nano/micro rough Al plate surface can be expressed as follows:

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

where Φ_s is the ratio of the area, which is in contact with the water droplet, to the surface area, which is in contact with air. θ is the water contact angle of the coated flat Al surface and θ^* is the water contact angle of the modified nano/microscale rough surface. The rough surface of the coated Al plate contains air, which prevents the permeation of water into the spaces within the rough surface. The contact area between the coated rough surface and the water droplet significantly reduced because of the trapped air in the valley of the rough space. The water contact angle of the untreated Al plate coated with HAHTP polymer was 81.5° , and that of the Al plate modified with HAHTP polymer after the chemical etching was 154° . These two values of water contact angle were applied to the above equation. The value of Φ_s was calculated as 0.088. The significantly low value of Φ_s indicates that only 8.8% of the water droplet is in contact with superhydrophobic surface, and the rest of the water droplet is in contact with air. Thus, a very small area of contact exists between the superhydrophobic surface and water droplet, and a water droplet on the superhydrophobic surface easily rolls off.

Conclusion

HAHTP monomer was synthesized and used for the fabrication of a superhydrophobic Al surface after chemically etching the Al alloy followed by coating with HAHTP monomer and polymerization. The chemical etching created a nano/microscale rough surface on which the monomer, HAHTP, was coated and then polymerized. The SEM images of the Al surface show no change in the morphology

after the polymerization. The superhydrophobicity of the Al surface can be attributed to the ideal structure of the surface and the coating with HAHTP polymer. The polymer of HAHTP acted as a low-surface-energy material, for the fabrication of superhydrophobic surface. Thus, HAHTP has great potential for the fabrication of artificial biomimetic surfaces in the future.

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