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Robust Superhydrophilic/Hydrophobic Surface Based on Self-Aggregated Al_2O_3 Nanowires by Single-Step Anodization and Self-Assembly Method

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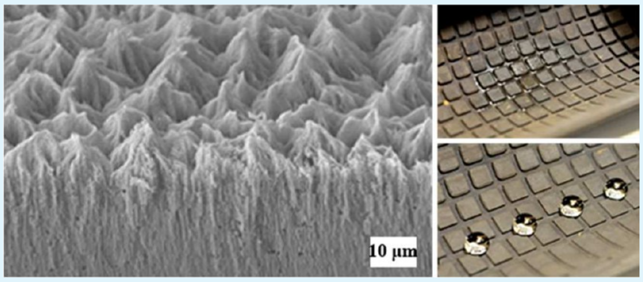
Ⓢ *Supporting Information*

ABSTRACT: Superhydrophilic and superhydrophobic surfaces were studied with an eye to industrial applications and use as research tools. Conventional methods involve complex and time-consuming processes and cannot feasibly produce large-area three-dimensional surfaces. Here, we report robust and large-area alumina nanowire structures with superhydrophobic or superhydrophilic properties, generated by an inexpensive single-step anodization process that can routinely create arbitrary three-dimensional shapes. This process is expected to open up diverse applications.



KEYWORDS: *robust superhydrophobic surface, superhydrophilicity, superhdrophobicity, alumina nanowire, anodization, self-assembly method*

Surface wetting properties, especially superhydrophobicity and superhydrophilicity, have generated considerable interest in the relatively new field of nanotechnology as a result of their nonwetting and wetting properties. Superhydrophobic surfaces, which have a contact angle (CA) with a water droplet greater than 150°, have been used in a lab-on-a-chip and microfluidic devices,[1,2] and have the capability for diverse industrial applications including self-cleaning,[3] water drag reduction on the inner surface of macro pipes and outer walls of vehicles,[4] and anti-icing/deicing effects.[5] Superhydrophilic surfaces, with a contact angle of almost 0°, also have practical advantages including an outstanding defogging effect, and enhanced heat transfer on boiling and evaporation because of the increased surface contact area between water droplets and the roughened surface.[6−8] Superhydrophobic or superhydrophilic surfaces can be produced by modifying the surface energy and creating a rough surface. These surfaces both have enhanced roughness, such as nanotextured or hierarchical micro/nanostructured surfaces like the lotus leaf.[4,9−17] The wetting (or nonwetting) properties depend on their surface energy,[18−22] which should be lower than that of water for superhydrophobic surfaces and higher for superhydrophilic ones. Various methods for controlling the roughness and the surface energy have been developed so as to give the desired wetting properties. These include lithography,[23,24] laser/plasma etching,[25,26] electrochemical etching,[4,27,28] sol−gel method,[29,30] phase separation,[31] chemical vapor deposition,[32] and deposition of nanoparticles.[15,33] These methods all involve complex and time-consuming processes and cannot readily be adapted to produce large-area three-dimensional surfaces.

To overcome these shortcomings, polymer replica methods have been proposed, based on a nanoporous template such as anodic aluminum oxide (AAO).[4,16,34,35] These methods can produce large-area three-dimensional surfaces, but are not readily applied to create complex shaped structures or maintain wettability under external pressure, because of the low mechanical strength of the replicated polymer nanowires. It is therefore important to develop novel techniques that would allow the inexpensive fabrication of large-area robust superhydrophobic or superhydrophilic surfaces having complex shapes.

Below, we report robust and large-area alumina nanowire structures with superhydrophobic or superhydrophilic properties, fabricated by an inexpensive single-step anodization process that can be used to prepare arbitrary shapes. To fabricate micro/nanostructured alumina nanowires (MNSANs) having greater surface energy than water so as to have superhydrophilic properties, we anodized an Al surface under specified conditions for 10 min. This creates nanoholes with a capillary effect on the Al surface, and also transforms the upper nanoholes to nanowires with an increased roughness. These nanowires were self-aggregated due to their high aspect ratio; they formed microstructures and eventually became hierarchical

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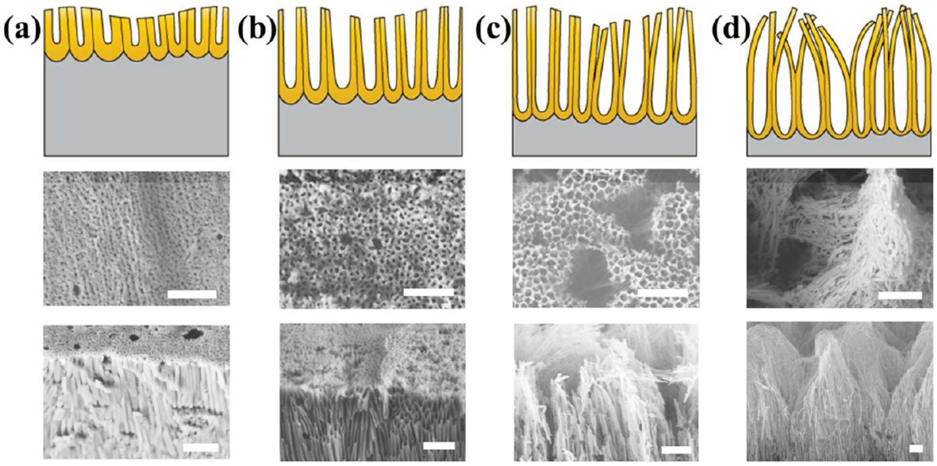

Figure 1. Formation of micro/nanostructured alumina nanowires on nanoporous anodic aluminum oxide. (a−d) Anodization time is respectively 1, 3, 5, and 10 min. (Scale bar: 1 μm).

micro/nanostructures. The measured CA of water with this surface was almost 0°, because of both the high surface energy and the increased roughness of the alumina nanowires. A superhydrophobic surface was created in 10 min as a self-assembled monolayer on the MNSANs, using a hydrophobic polymer with low surface energy. The measured modulus and hardness of the MNSANs were more than 700 times greater than those of polymer nanowires, and it was possible to maintain their superhydrophobicity or superhydrophilicity without deformation under external pressure. Furthermore, the method was successfully demonstrated as producing a three-dimensional superhydrophobic/superhydrophilic surface within 30 min, of arbitrary shape and area.

Because AAO nanostructures with uniform nanoholes are easily fabricated using an electrochemical process with no obvious size limitation, they have been used extensively in various applications. Anodizing technologies for forming nanoholes of various sizes and porosities are well-established.[36] During the formation of alumina (i.e., aluminum oxide) on the surface of Al in the anodizing process, the alumina volume is increased. As a result, the alumina nanohole structures become self-organized into a hexagonal close-packed pattern that generates minimum stress. The alumina nanohole structures have enhanced wettability because of the hydrophilicity of alumina and the increase in the surface roughness. However, because of insufficient surface roughness on the nanohole structure, with porosity less than about 10%, further processes are necessary to create superhydrophilicity. These include a widening process to increase porosity[16] and a way of generating microroughness.[28,37] On the other hand, a hierarchical micro/nanostructure with superhydrophilic properties can easily be fabricated by the single-step anodizing process using our method. Anodization is performed on industrial Al (99.5%) in 0.3 M oxalic solution at a constant voltage of 65 V, using a computer power supply (Digital Electronics Co., DRP-92001DUS). The solution was maintained at 27 °C during anodization by a circulator (Lab. Companion, RW-0525G). In this condition, nanoholes were formed on the Al substrate for the first minute, as in the previous anodizing process; see Figure 1a. These nanoholes were gradually etched and widened as the anodizing continued, however. The nanoholes increase in size and the walls enclosing the nanoholes become thinner (See Figure 1b). After 5 min, some parts of the nanoholes have been completely etched away, because of the nonuniform thickness of the walls; microscale valleys are created, as in Figure 1c. The remaining nanoholes on the top surface have entirely vanished and the walls enclosing the nanoholes are transformed into nanowires. After 10 min, the upper part of alumina nanoholes is entirely transformed to nanowires with hierarchical micro/nanoroughness, maintaining the nanohole structures at the lower part, as shown in Figure 1d. Consequently the MNSANs, with significantly increased roughness, and the high surface energy for superhydrophilicity, are self-aggregated on nanohole structures in 10 min by single-step anodization. The top view and a cross-sectional view at specific anodizing times were captured by a field emission scanning electron microscope (FE-SEM; JEOL JSM-7401F, NCNT).

Subsequently, the anodization process was performed for 1 h to ensure that the topography changes with the anodizing time. The anodization process proceeds, maintaining the thickness of both the upper alumina nanowires and the lower alumina nanohole, and also the topography of hierarchical micro/nanoroughness (see Figure 2a,b). It is confirmed that an anodizing time of 10 min is sufficient to create a surface with hierarchical micro/nanoroughness. To generate a superhydrophobic surface, the surface of the MNSANs was modified using a hydrophobic self-assembled monolayer (heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane, HDFS) to give a lower surface energy while maintaining the surface roughness. Topography of the HDFS coated surface is shown in Figure 2c,d which are cross-sectional view and top view, respectively. The MNSAN specimens were dipped in a mixture of n-hexane and HDFS (volumetric ratio 1000:1) for 5 min. They were then washed with distilled water and dried by nitrogen gas. There were few changes in the surface topography from before to after coating, as shown in Figures 2a−d.

To study the wetting or nonwetting properties of the specimens, the contact angles with water were measured using a drop shape analysis system (DSA-100, Kruss Co.), with droplets of size 3 μL at room temperature. The mean contact angles of the prepared specimens were determined by measuring the same sample in ten different positions. As the anodizing time increases, the hydrophilicity also increases, as shown in Figure 3. This implies that the wetting property gradually increases as the upper part of the nanohole structures becomes transformed into the nanowires structure. As a result,

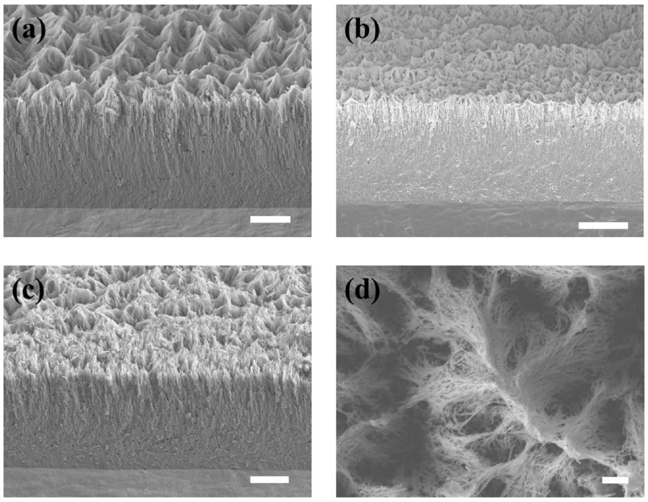

Figure 2. SEM images showing the thickness of the anodized Al surface after differing anodization times, and HDFS coated surface. (a) Cross-section view of anodized Al (anodization time: 10 min). (b) Cross-section of anodized Al (anodization time: 1 h). (c) Cros-section of anodized Al with HDFS. (d) Top view of anodized Al with HDFS. (c, d) Anodization time: 10 min. (Scale bar: (a−c) 10 μm, (d) 1 μm).

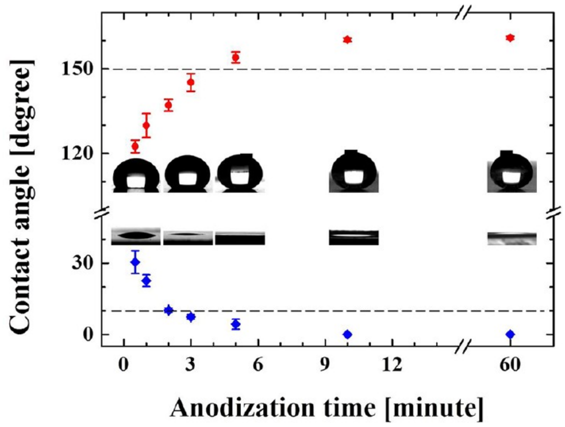

Figure 3. Surface contact angles according to anodization time. As time increases, the hydrophilicity is increased and the corresponding hydrophobicity is also increased. The surface has superhydrophilicity after 3 min and exhibits superhydrophobicity after 5 min of anodization.

the MNSAN structure anodized for 10 min exhibits superhydrophilicity, having near-zero contact angle. The wettability is greatly enhanced because the actual contact area between water droplets and the surface increases owing to the MNSAN structures that have self-aggregated on the nanohole structures. Also, the lower part of the nanoholes may further increase wettability by the capillary effect, which pulls water into the nanoholes.[6−8]

For specimens coated with hydrophobic polymer, the hydrophobicity also increases with the anodizing time. This means that the surface wettability depends on the surface energy for a surface of given topography. In the case of superhydrophobic surfaces, the MNSANs and nanoholes contain trapped air between the nanostructures.[38] This trapped air reduces the actual contact area between the water droplets and the surface, so that the surface exhibits superhydrophobicity.

To verify the robustness of the superhydrophobic surface with HDFS coating, we looked at its mechanical properties. We have evaluated the robust surface of a flat Al, Teflon nanowires and the present superhydrophobic surface. The Teflon nanowires surface was fabricated by anodization and replication with Teflon (Teflon AF 601S2, 6 wt %).[4] Figure 4 shows the modulus and surface hardness of the resulting surfaces. A TriboScope nanoindenter (Hysitron Inc.) was used for these tests, with a Berkovich tip. In flat Al, modulus is 92.15 GPa and hardness is 1.05 GPa. The modulus of the alumina nanowires is 103.8 GPa and its hardness is 5.41 GPa. The value of Teflon nanowires is 96 and 7 MPa, respectively. Relative to the Teflon nanowires, the modulus of the alumina nanowires is about 1000 times larger and 700 times harder. The mechanical property tests show that the alumina nanowires structure is strong enough to resist external pressure and maintain superhydrophobicity better than other superhydrophobic surfaces. This is crucial to broadening the applications of superhydrophobic surfaces.

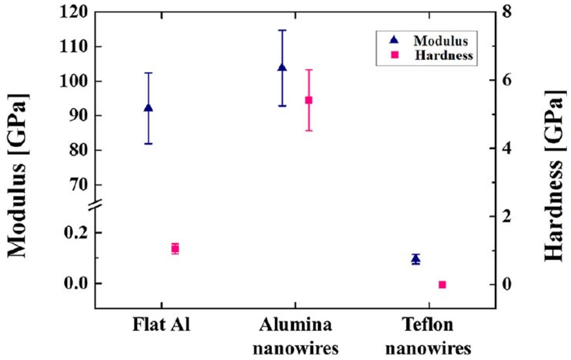

Figure 4. Indentation modulus and surface hardness of flat Al, alumina nanowires, and Teflon nanowires. The modulus and hardness of the alumina nanowires surface are greater than for the flat Al and Teflon nanowires surface.

The present method is applicable regardless of sample shape or size, because the ions generated by the anodization process can move freely in any direction and the specimen to be anodized can readily be made to any shape.[39,40] The fabricated sample is shown in Figure 5. The diameter of the specimen is 70 mm and the cylinder is 210 mm in length. A superhydrophilic or superhydrophobic surface can be fabricated by anodization and the HDFS coating method within 30 min. Figure 5a−d show a superhydrophilic surface with 0 °CA; the water droplet size is 50 μL. The water droplet spreads immediately along the surface structures, because the surface energy is larger than the surface tension of the water droplet. This phenomenon is shown at the inner and outer side of the sample in the Supporting Information, movies S1−S3. Figure 5e−h shows the superhydrophobic surface with CA greater than 150°. The size of the water droplets is 30 μL in Figure 5e, f, and h, but only 10 μL in Figure 5g because heavy droplets tend to roll along curved surfaces more than small droplets. Water droplets form into beads and roll along a superhydrophobic surface because the surface energy is less than the surface tension of the water droplet. This phenomenon is shown in the Supporting Information, movies S4−S6.

In summary, we have successfully fabricated robust, large-area, three-dimensional superhydrophobic and superhydrophilic surfaces using a single-step anodization method. As a

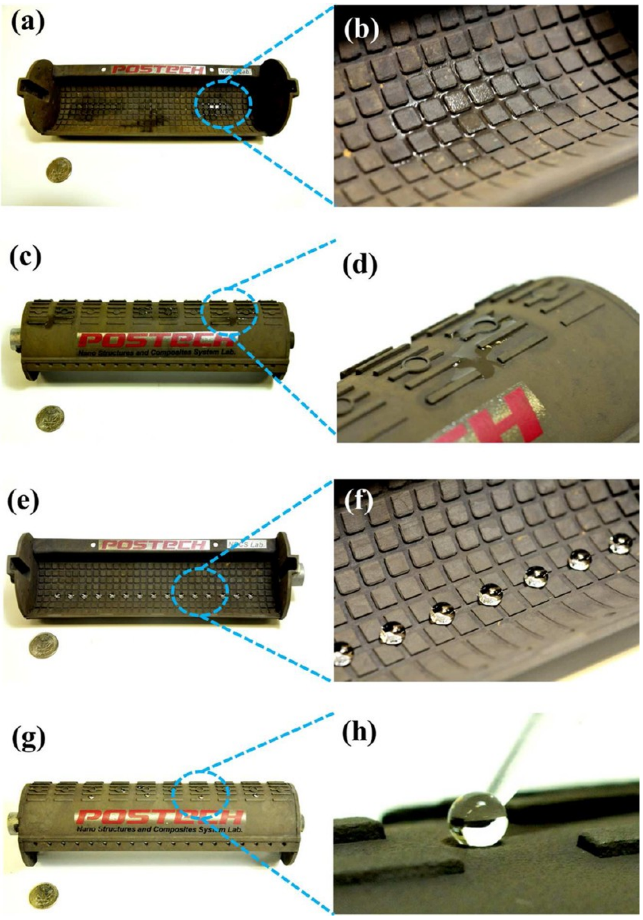

Figure 5. Complex shaped alumina surface. A one-quarter coin was included for size comparison. (a−d) and (S1−S3) Superhydrophilic surface. (e−h) and (S4−S6) Superhydrophobic surface. Superhydrophilic and superhydrophobic surfaces were successfully fabricated regardless of the specimen size or shape.

result of anodization, nanoholes and MNSANs are produced; these structures have superhydrophobic or superhydrophilic properties according to the surface energy, because the structures maximize surface wetting. The method is simple, rapid and inexpensive, and can be used without embellishment in industrial applications, starting from Al specimens of any size or shape. The resulting superhydrophobic or superhydrophilic surface also has excellent mechanical properties, as characterized by modulus and hardness, in comparison with polymer replicated superhydrophobic surfaces. We expect that applications of superhydrophobic and superhydrophilic surfaces will be facilitated by this method.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Movies about water droplet behavior on three-dimensional superhydrophilic and superhydrophobic surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

CA, contact angle; AAO, anodic aluminum oxide; MNSANs, micro/nanostructured alumina nanowires; HDFS, heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane

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