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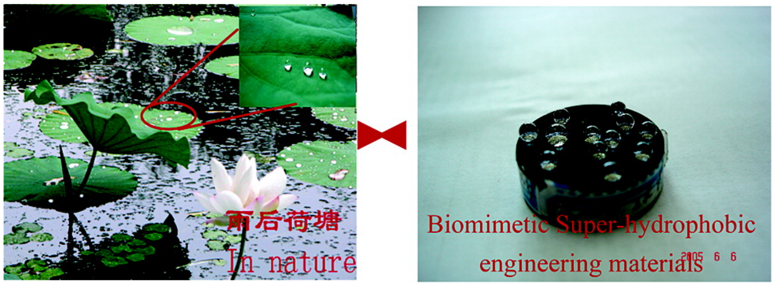

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Stable Biomimetic Super-Hydrophobic Engineering Materials

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The studies of materials with super-hydrophobic surfaces,[1−3] such as the smart surfaces that are able to switch between super-hydrophilicity and super-hydrophobicity by various triggers,[1e] have widely attracted attention due to their unique surface microstructure and physicochemical properties. Wettability is a very important aspect of materials and is governed by both the surface chemical composition and geometric structure.[1−5] A closely related phenomenon in nature is the "lotus-effect", referring to surfaces that are difficult to wet [for super-hydrophobicity, the water contact angles are larger than 150°[3]], which can be found in the leaves of lotus, taro, and haulm, etc.[2] These surfaces usually have binary structures at both micrometer and nanometer scales, which makes it possible to trap a large amount of air and to minimize the real contact area between surfaces and water droplets. Coating materials such as nanoscale films with very low surface energy on surfaces is the key factor for constructing super-hydrophobic surfaces. Bearing this in mind, we aim to biomimetically construct artificial super-hydrophobic surfaces that may have numerous technical applications[4] in resisting water coalescence,[1a,2b,c,5] fog condensation,[6] and preventing contamination,[1c,7] while increasing biocompatibility,[8] lubricity, and durability.[9]

The design of biomimetic super-hydrophobic surfaces with long-term stability by means of a simple and inexpensive method is reported here. Super-hydrophobic surfaces were fabricated with engineering materials of aluminum and its alloy using sodium hydroxide (NaOH), perfluorononane (C_9F_{20}), and poly(dimethylsiloxane) vinyl terminated (PDMSVT) containing 1 wt % 184 curing agent (dimethyl methylhydrogen siloxane, sylgard 184, one part of commercial precursor of silicone elastomer, Dow Corning Co.). The chemical composition of aluminum alloy (2024Al) includes 92.81 wt % aluminum, 5.51 wt % copper, and 1.68 wt % magnesium. Pure aluminum and its alloy were selected because of their diverse technological applications in the auto, aviation, and space industries.[10]

The method employed is as follows: Blocks of Al and its alloy ($\Phi = 24 \times 8$ mm^2, $R_a = 0.1$ μm) were ultrasonically cleaned in alcohol and deionized water baths, respectively. After drying, the blocks were immersed in 1 M NaOH solution for 2 h, rinsed with deionized water again, and then oven dried at 120 °C for 1 h. The Al block was modified with C_9F_{20}, and the aluminum alloy was coated with PDMSVT. The C_9F_{20} and PDMSVT films were obtained by spin-coating at a speed of 3000 rpm for 30 s and annealed in a vacuum oven at 80 °C for 2 h. The thickness of the single-layer C_9F_{20} film (if stand) on aluminum was calculated to be about 2 ± 1 nm.[11]

Aluminum and its alloys are hydrophilic materials with a native oxidized layer that has a contact angle (CA) of about 67° for water. The as-prepared super-hydrophobic surfaces on aluminum and its alloy have water CAs of 168 ± 2 and 161 ± 2°, respectively, as shown in Figure 1 (for movies of the super-hydrophobic surfaces, see Supporting Information). The sliding angles are both lower than 5°, implying that the water droplets could be moved upward easily even when the surfaces were only slightly tilted. Interestingly, the as-prepared surfaces show super-hydrophobic properties in the pH range from 1 to 14, that is, the CAs are larger than 150° for not only water but also corrosive liquids, such as acidic and basic aqueous solutions.

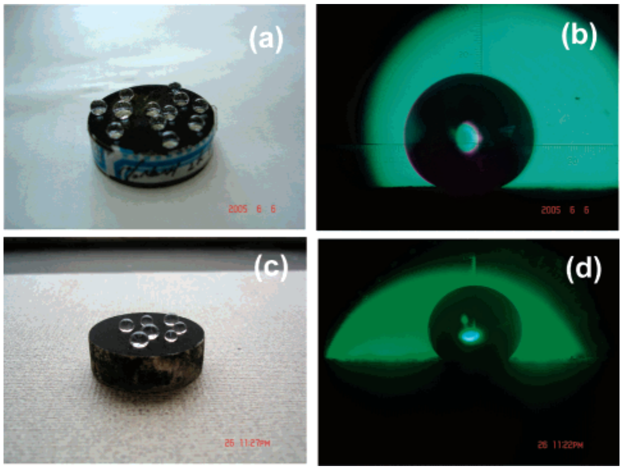

Figure 1. (a) Optical image of water droplets with different sizes on the surface of Al block treated with C_9F_{20}. (b) Profile of one water droplet on the surface having a CA of 168 ± 2°. (c) Optical image of water droplets with different sizes on the surface of super-hydrophobic aluminum alloy modified with PDMSVT. (d) Profile of the water droplet with a CA of 161 ± 2°.

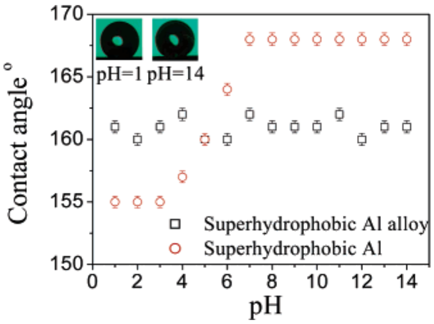

Figure 2. The relationship between pH and contact angle on the super-hydrophobic surfaces of aluminum and its alloy, respectively.

Figure 2 shows the relationship between pH and CA on the super-hydrophobic surfaces. CAs on the super-hydrophobic aluminum surfaces remained unchanged (155 ± 2°) within experimental error when the pH varied from 1 to 3. The CAs changed from about 157 ± 2 to 168 ± 2° when the pH increased from 4 to 7. At pH > 7, the CAs remained constant at 168 ± 2°. For the super-hydrophobic aluminum alloy, there was no obvious fluctuation of the CAs, within

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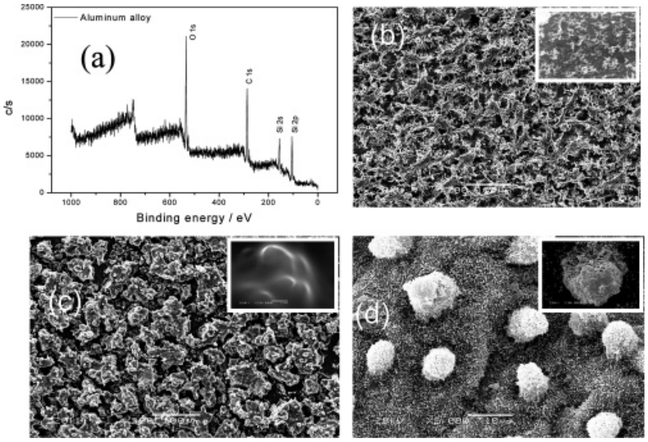

Figure 3. (a) XPS spectra of PDMSVT films on aluminum alloy surfaces. (b) SEM image of Al surfaces treated with NaOH and C_9F_{20}; bar represents 100 μm. The inset is a larger magnification with bar = 0.5 μm. (c) SEM image of aluminum alloy surfaces modified with NaOH and PDMSVT, bar represents 100 μm. The inset is a larger magnification with bar = 1.0 μm. (d) SEM image of lotus surfaces, bar represents 10 μm. The inset is a larger magnifications with the bar = 1.0 μm.

the error, over the pH range from 1 to 14. All the CAs were in the range of 160 to 162°, indicating that the pH of the aqueous solution had little or no effect. These results are very important for the use of aluminum and its alloy as engineering materials with super-hydrophobic surfaces in the wide pH range of corrosive liquids. Hopefully, such special super-hydrophobic properties will greatly extend the applications of aluminum and its alloy in many other important industrial fields, especially as solid lubricating materials (see Supporting Information for friction coefficient tests). The insets to Figure 2 show the shapes of aqueous solution droplets with pH = 1 and 14, respectively, on aluminum and its alloy. The two droplets remain as spheres with CAs larger than 150, 155 ± 2, and 168 ± 2°, respectively. High CAs for both acidic and basic aqueous solution droplets on any kind of solid surfaces, to the best of our knowledge, have only been reported on nanostructured polyacrylonitrile (PAN) films prepared by the template-based extrusion method,[12] which showed super-hydrophobic properties in the pH range from 1.07 and 13.6. Compared with the method we describe herein, super-hydrophobic nanostructured polyacrylonitrile (PAN) films are expensive and complex.

The super-hydrophobic properties were tested at different time intervals. After 3 months of storage in air, the values of the contact angles remained essentially constant, indicating that the biomimetic super-hydrophobic surfaces have long-term stability. We further studied the durability by soaking the surfaces in water, acidic, and base solutions for several hours and found essentially no change of water contact angle.

Figure 3a shows the XPS spectra of a PDMSVT film on aluminum alloy. No absorbance was ascribed to aluminum, but the absorbances of Si, C, and O demonstrate that all aluminum alloy surfaces were covered by the cross-linked PDMSVT film. This film has intrinsic properties of chemical resistance, so it can be used in acidic and basic liquids.

The super-hydrophobicities are believed to be due to the presence of cooperative binary structures at micro- and nanometer scales, which reduce the energies of the surfaces.[1−3] These micro- and nanometer scale structures were demonstrated by scanning electron microscopy (Figure 3 b−d; also see Supporting Information for larger figures) of the surface morphologies of Al, aluminum alloy, and lotus leaves. Figure 3b shows the typical morphology of the super-hydrophobic surface on aluminum, clearly showing porous structures with wall thicknesses of 0.8−1 μm and pore diameters of 300−600 nm. Figure 3c is the SEM image of the super-hydrophobic surface on aluminum alloy, which is very similar to that on Al. Islands with diameters of 10−50 μm are distributed uniformly across the surface. The two images clearly indicate that the super-hydrophobic surfaces of Al and its alloy modified with C_9F_{20} and PDMSVT have binary structures. Both structures in Figure 3b and c are greatly similar to lotus surfaces (Figure 3d). Such structures can trap a large amount of air, inducing CAs of more than 160°.[1,3,8] The insets to Figure 3b−d are the subsurface images at 10 000X magnification, implying the subsurfaces are composed of rods with diameters of 50−100 nm on the Al surface and nanoconvexities with diameters of 20−100 nm in arrays on the islands.

In conclusion, we have demonstrated a simple and inexpensive method to create super-hydrophobic surfaces on aluminum and its alloy. The super-hydrophobic surfaces show long-term stability over a wide pH range, that is, not only for pure water but also for corrosive liquids including acidic and basic solutions. We expect that this technique will make it possible for large-scale production of super-hydrophobic engineering materials with new industrial applications.

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Supporting Information Available: Movies of the sliding of water/aqueous solution droplets on super-hydrophobic surfaces, SEM images at larger magnification of aluminum and its alloy's surface morphologies, and tribological properties of the as-prepared surface of aluminum alloy (2024Al). This material is available free of charge via the Internet at http://pubs.acs.org.

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