1. Introduction

The wettability of solid surfaces is one of the most important aspects in both theoretical research and industrial applications. One extreme case of wettability properties, namely superhydrophobic surfaces with a water contact angle (CA) greater than 150°, has aroused considerable interest from many researchers in recent years because of the novel aspects of surface physics and important applications ranging from self-cleaning materials to microfluidic devices. Water droplets on smooth and flat hydrophobic solid surfaces do not usually form angles over 120° even on surfaces with very low surface free energy. Water droplets on superhydrophobic surfaces, however, will not come to rest and simply roll off if the surface is tilted even slightly. Such surfaces with low-contact-angle hysteresis are referred to as self-cleaning surfaces and the contamination on them is easily removed by rolling droplets and as such this type of surface has obviously great potential uses, as water will not “stick” to it. In nature, superhydrophobicity has been adopted by some plants, such as Nelumbo nucifera (L.) druce and is known as the Lotus effect.

Herein, we report a novel mixed-solution system for the fabrication of superhydrophobic surfaces on steel, copper alloy, and titanium alloy by a chemical etching method. The procedure was fairly facile to operate and no special technique or equipment was required. Moreover, the procedure is time-saving and superhydrophobic surfaces can be obtained within several hours. The reagents are cheap and the as-fabricated superhydrophobic surfaces are very stable. The substrate was easily varied from steel, copper alloy, and titanium alloy to other engineering materials. Therefore, a highly effective, inexpensive, simple and convenient to operate method that would be very advantageous for industrial large-scale production is needed.

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2. Results and Discussion

Steel and copper alloy are hydrophilic materials with a native oxidized layer that have a contact angle far less than 90° for water. To achieve a superhydrophobic surface, a rough substrate is prerequisite, as the hydrophobic property can be am-
plified by the roughness.[17,18] Here a nitric acid and hydrogen peroxide mixed-solution system was employed as the etching reagent on the engineering materials to obtain the rough surfaces. Fluoroalkylsilane was used as a hydrophobic material to reduce the surface free energy. The blocks of steel and copper alloy were immersed in the etching solution for several minutes, followed by washing and immersion in a methanol solution of fluoroalkylsilane. After etching and fluorination, the as-prepared superhydrophobic surfaces on steel and copper alloy have water CA of 161° ± 1° and 158° ± 1°, respectively, as shown in Figure 1. The water droplets do not rest on the surface, and they easily roll down the blocks even when there is only little or no apparent tilt of the surfaces (< 2°), which makes it very difficult to measure the CA. Interestingly, falling water droplets can bounce from both the as-prepared steel and copper alloy surfaces. After several more bounces, the droplets eventually roll off without ever coming to rest on the surface, implying the contact-angle hysteresis is low.

The as-prepared surfaces show superhydrophobic properties in the pH range from 1 to 14, that is, the contact angles are larger than 150° not just for pure water but also for corrosive liquids, such as acidic, basic, and some aqueous salt solutions. Figure 2 shows the relationship between the pH and CA on the superhydrophobic surfaces. CAs on the superhydrophobic steel surfaces remained unchanged (155° ± 1°) within experimental error when the pH varied from 1 to 2, changed from about 156° ± 1° to 158° ± 1° when the pH increased from 3 to 6, and remained constant at 161° ± 1° when the pH increased from 6 to 10. At >pH 10, the CAs show little fluctuation. For the superhydrophobic copper alloy surface, the fluctuation of the CA with pH is similar to that for the superhydrophobic steel surface. Steel surfaces with high contact angles for bare salt solutions would greatly extend the application of steel in many industrial fields, especially as marine engineering materials. Thus, the relationship between the concentration of aqueous salt solutions (NaCl and Na2CO3) and the CA on superhydrophobic steel surfaces was also measured. The CAs remained in the scope of 156°–160° ± 1° within experimental error when the concentration varied from 0.01 to 2 M. These results are very important for the use of steel and copper alloy as engineering materials with superhydrophobic surfaces in the wide pH range of corrosive liquids.

To evaluate the stability of the as-prepared superhydrophobic surfaces, they were tested at different time intervals. After exposure in air for two months, the values of the contact angles still remained constant, indicating that the as-prepared superhydrophobic surfaces have long-term stability. Further the as-prepared surfaces were immersed in water for several hours to study the durability and essentially no change in the water contact angle was found.

In this acid and hydrogen peroxide mixed-solution etching system the substrate was easily varied, thus a superhydrophobic titanium alloy surface was also fabricated. The titanium alloy was etched by a hydrofluoric acid and hydrogen peroxide mixed solution followed by surface fluorination. The as-prepared superhydrophobic surface of titanium has a water CA of just over 150° (Fig. 5d).

Figure 3 shows the X-ray photoelectron spectroscopy (XPS) data of the as-prepared superhydrophobic steel surface. A strong fluorine peak located at 688 eV and also the peaks of Si, C, and O were observed in this case. This demonstrated that the steel surface was covered by the fluoroalkylsilane film which greatly reduced the free energy of the surface. The XPS spectra of the as-prepared superhydrophobic copper alloy and titanium alloy surfaces were quite similar to that of the superhydrophobic steel surface (see Supporting Information).

The superhydrophobicities are believed to be due to the presence of synergistic binary geometric structures at the micro- and nanometer scale, which reduce the energy of the

Figure 1. a) Image of water droplets with different sizes on the as-prepared superhydrophobic surface of steel. b) Profile of a water droplet on the steel surface having a CA of 161° ± 1°. c) Image of water droplets with different sizes on the as-prepared superhydrophobic surface of copper alloy. d) Profile of a water droplet on the copper alloy surface with a CA of 158° ± 1°.

Figure 2. The relationship between pH and contact angle on the superhydrophobic surfaces of steel and copper alloy.
When the alloy substrates were immersed in the etching solution, the surface reacted with the acid vigorously. Because the alloys are made of different metals, the etching rates at different positions of the surface were unequal. Thus, surfaces with cavities and island structures were obtained. The continuous physical erosion by air bubbles generated on the interface of the alloy surface and the solution on the alloy surface might also be important.[19] The geometric microstructures formed on the substrates have been observed carefully by scanning electron microscopy (SEM) of the surface morphologies of steel, copper alloy, and titanium alloy (see Supporting Information for the SEM images of the unetched polished surfaces). Figure 4a and b show the typical porous morphology of the superhydrophobic surface on steel. Cavities with diameters of 20–30 μm and islands with diameters of 5–10 μm are distributed uniformly across the surface and increased the surface roughness. Figure 4b is very similar to the lotus-leaf surface whose structure can trap a large amount of air.[8] A further observation shows a flocy nanometerscale morphology on the islands and cavities. As shown in Figure 4c and d, “sting”-like with the width of 50 nm and length of 300–500 nm gave the surface its flocy appearance and made the air fraction of the interfacial areas high enough. Figure 5a, b, and c are the SEM images of the superhydrophobic surfaces on copper alloy (a,b) and titanium alloy (c), and these also show the cavities and the islands structures. Figure 5b shows a furrowlike structure with widths of several hundreds of nanometer in the superhydrophobic surface of the copper alloy. Figure 5c is very similar to the SEM images of superhydrophobic surfaces that are created from amphiphilic poly(vinyl alcohol) and aligned polyacrylonitrile nanofibers.[5] These images clearly indicate that the superhydrophobic surfaces of steel and copper alloy modified with $\text{CF}_3\text{(CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$ have binary geometric structures at the micro- and nanometer scale. No obvious nanometerscale structures were observed on the titanium alloy surfaces. The fluorinated binary structures or the micrometerscale structures have probably already trapped enough air to prevent the penetration of water droplets into the grooves, which bestowed the superhydrophobicity on the surfaces.

This observation can be explained by Wenzel’s law

$$\cos \theta_1 = r \cos \theta$$

first derived by Wenzel to describe the CA for a liquid droplet at a rough solid surface. $\theta_1$ and $\theta$ are, respectively, the water CA on a rough surface and smooth surface made of the same material, and $r$ is the roughness factor. This equation indicates that with increasing surface roughness, the actual CA decreases for hydrophilic materials ($\theta < 90^\circ$) and increases for hydrophobic materials ($\theta > 90^\circ$). Clearly, the CA for water will increase

\[\text{Figure 3. XPS spectrum of the fluoroalkysilane film on the superhydrophobic steel surface.}\]

\[\text{Figure 4. SEM images at different magnifications of the etched steel treated with fluoroalkysilane, the scale bars represent: a) 50 μm, b) 5 μm, c) 2 μm, and d) 500 nm.}\]

\[\text{Figure 5. SEM images at a) low and b) high magnifications of the etched copper alloy treated with fluoroalkysilane, the scale bar represents 20 μm and 1 μm, respectively. c) SEM image of the etched titanium alloy treated with fluoroalkysilane, the scale bar represents 5 μm. d) Profile of a water droplet on the superhydrophobic titanium alloy surface having a CA of 151°±1°.}\]
on the rough surface created by the cavities and islands. Fluoroalkylsilane is a typical intrinsically hydrophobic low-surface-energy material. The surface-modification with fluoroalkylsilane can be viewed as having a wax layer on the surface. After the modification, the water droplet cannot get into the cavities of the surface as air fills the cavities.

To fully understand the superhydrophobicity of the etched alloy surfaces modified with fluoroalkylsilane, we also described the contact angle in terms of the Cassie equation\[21\]

$$\cos \theta = f_1 \cos \theta_1 - f_2$$

which is generally valid for heterogeneous surfaces composed of air and a solid with superhydrophobicity. Here, $\theta_1$ (161°) is the contact angle of the superhydrophobic steel surface; $\theta$ (109°) is the contact angle of the smooth steel surface modified with fluoroalkylsilane; and $f_1$ and $f_2$ are the fractional interfacial areas of the porous microstructures and of the air in the interspaces among the porous microstructures, respectively (i.e., $f_1 + f_2 = 1$). This equation predicts that increasing the fraction of air ($f_2$) should increase the contact angle of the porous film ($\theta$). According to the equation, the $f_2$ value of the rough surface with porous microstructures is estimated to be 0.92. This means that air occupies about 92% of the contact area between the water droplet and the porous microstructures, which is responsible for the superhydrophobicity of the surface.

3. Conclusion

We fabricated superhydrophobic surfaces on common industrial steel, Cu alloy, and Ti alloy by utilizing wet chemical etchants and surface coating with fluoroalkylsilane. Compared with the traditional methods, it is convenient, time-saving, and inexpensive. The as-fabricated superhydrophobic surfaces show long-term stability even under application of corrosive liquids including acidic, basic, and salt solutions. The superhydrophobic surfaces are able to withstand salt solutions in a wide range of concentrations, which may open a new avenue in applications especially for the marine engineering materials where salt resistance is required. We expect that this technique will accelerate the large-scale production of superhydrophobic engineering materials with new industrial applications.

4. Experimental

Blocks of steel (96.30 wt % iron, 1.34 wt % chromium, 1.33 wt % carbon, 1.03 wt % manganese) and Cu alloy (91.92 wt % copper, 8.08 wt % tin) with a size of $U = 24 \times 8 \text{ mm}$ were polished and ultrasonically cleaned in alcohol and water. Then they were etched by immersion in a HNO$_3$ (65 wt %) and H$_2$O$_2$ (30 wt %) mixed solution (v/v, 1:1) in beakers at room temperature. The etching time is 6 min for steel and 3 min for Cu alloy. Titanium alloy (TC4, 15 mm × 20 mm × 0.5 mm) was etched by immersing in a HF (40 wt %) and H$_2$O$_2$ (30 wt %) mixed solution (v/v, 1:1) in beakers at room temperature for 5 min. After etching, the substrates were immediately rinsed ultrasonically with water and washed with deionized water, followed by drying in a stream of N$_2$ and then in an oven at 80°C for 30 min.

A methanol solution (1.0 wt %) of CF$_3$(CF$_3$)$_2$CH$_2$SH$_2$(OCH$_3$)$_3$ (ABCOR GmbH & Co. KG, Germany) was hydrolyzed by the addition of a threefold molar excess of water at room temperature. The etched alloy substrates were immersed in the hydrolyzed silane solution for 2 h at room temperature. After removal from the solution, the substrates were heat treated at 140°C for 1 h.

Contact angles were measured with an optical contact angle meter at ambient temperature. Water droplets were dropped carefully onto the surfaces and the average value of five measurements at different positions of the sample was adopted as the contact angle. The roll-off angle is defined as the angle at which the water droplet begins to roll off the gradually inclined surface. The superhydrophobic surfaces were observed by SEM (SEM-S5600LX, KEVEX) and filed-emission (FE)-SEM (S-4800, Hitachi) to characterize their morphology. XPS analyses of the samples were performed on a PHI-5702, Physical Electronics, Inc.) spectrometer using an AlK$_x$ X-ray source (1486.7 eV). The energy scale was internally calibrated by referencing to the binding energy (E$_b$) of the C1s peak of a carbon contaminant at 284.5 eV.

Received: May 31, 2006
Revised: August 17, 2006
Published online: January 26, 2007


