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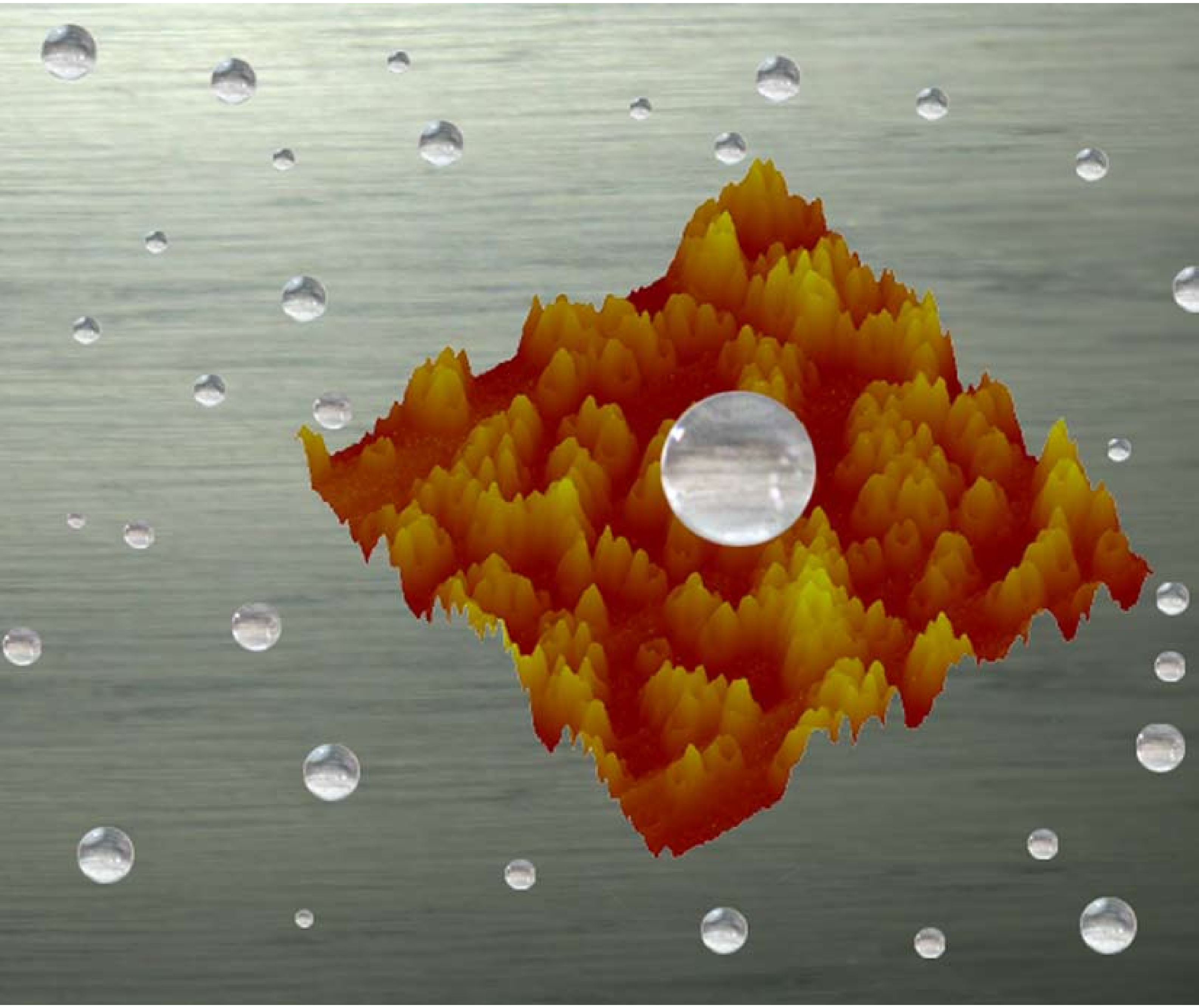

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PAPER
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A superhydrophobic coating on aluminium foil with an anti-corrosive property

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A superhydrophobic coating with an anti-corrosive property has been fabricated on aluminium foil by a simple sol–gel method with polystyrene spheres (PS) included as a removable template. The effects of the size of PS on the surface structure and the superhydrophobicity have been researched. When the size of PS is 200 nm, the prepared coating shows a high static water contact angle (CA) larger than 150° but also a large adhesive force with the substrate, and the water droplet can be pinned on the substrate tilted at any angle. When the size of PS is 500 nm, the prepared coating has a CA as high as 160°, and the water droplet can roll off the substrate easily. Under this circumstance, the coated aluminium foil is also found to possess good chemical stability and, in particular, an anti-corrosive property. Thus the CA remains nearly unchanged after exposure to air for one year or immersion in an acid solution for 5 h.

Introduction

The surface state of the aluminium foil used in radiators and condensers has a significant effect on the lifetime and energy consumption of air-conditioning facilities. In order to prolong the lifetime and reduce energy consumption, the surface of the aluminium foil is required to be both anti-corrosive and hydrophobic. Aluminium foil with ordinary hydrophobicity is unfavorable for the miniaturization of air-conditioning facilities, because water droplets can slide off the surface only when they reach a large size, and thus a large space between adjacent aluminium foils is needed to avoid the forming of water droplet bridges. Therefore, the surface of the foil is preferred to be superhydrophobic (SH) as tiny water droplets of even less than 10 μL can slide off such a surface.[1–3]

Generally, a surface with a water contact angle (CA) larger than 150° and sliding angle (SA) less than 10° can be called SH.[2–5] It has been found that a nano/micro-structure must be developed for achieving a SH property.[4–8] This is because a flat surface can have a CA no more than 120° even if its surface energy has been lowered by introducing groups of $-CF_3$, $-CH_3$ and $-CH_2-$.[4,9] Currently, excellent SH surfaces with elaborate nano/micro-structures are obtained by methods such as chemical vapor deposition,[10–14] colloidal self-assembly,[15–17] wet chemical etching,[18,19] electrospinning[20,21] and some others.[22,23] Specifically, several studies have reported the successful fabrication of a SH surface on aluminium by chemical etching.[19,24,25] However, chemical etching can not only impair the aluminium substrate but also decrease its anti-corrosive property.

In this study, considering the special working environment of radiators and condensers in air-conditioning facilities, we selected silica as the coating material due to its outstanding thermal and chemical stabilities. Both surfaces of an aluminium foil are coated by a sol–gel dip coating method with polystyrene spheres (PS) included as a removable template. We report that the CA of the silica coating can reach 160°, and a water droplet of 4 μL can roll off very easily. In addition, the coated aluminium foil possesses a high chemical stability and an anti-corrosive property. This is based on the observation that the CA remains nearly unchanged after exposure to air for a year or immersion in an acid solution for 5 h.

Experimental

Aluminium foils of 1.5 cm × 6 cm were used as substrates in all experiments. The surface contaminants of the substrate were cleaned by immersing it in NaOH solution with a pH value of 12 at 90 °C for 30 min and then rinsed by a large amount of pure water and dried in a vacuum oven. The cleaned substrate was dip-coated by a sol–gel containing 2.5 wt% silica colloid particles and 0.2 wt% PS. The PS was used as a removable template to control the surface roughness of the coating. Two types of PS with diameters of 200 and 500 nm were used separately. The withdrawing speed was kept at 2.65 cm min^{-1}. The substrate was immersed in the sol for 5 min before the first dip-coating but only 5 s before the following dip-coating. After each coating, the substrate was dried at room temperature (25 °C) for 5 min, and this step was repeated five times. Subsequently, the as-coated substrate was heat treated at 550 °C for 15 min to remove the PS. The surface free energy of the substrate was then lowered by chemical vapor deposition (CVD) of a monomolecular perfluoroalkylsilane (FAS). The pH value of the water solution used for measuring the CA was adjusted by acetic acid or NaOH. An acetic acid solution with a pH value of 3 was used to test the anti-corrosive property of the coated aluminium foil.

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The roughness and three-dimensional morphology of the surface were characterized by atomic force microscopy (AFM) (Multimode Nanoscope IIIa, USA). The CA and SA of a pure water droplet (18.2 MΩ cm in resistivity) on the surface were measured by a contact angle meter (OCA20, Germany) at ambient atmosphere and room temperature. Water droplets of 4 μL were placed slowly and carefully onto the surface, and the static CA was measured at different positions at least five times. The colloid particles of silica and PS were examined by transmission electron microscopy (TEM, JEM-2010, INCA OXFORD). The chemical compositions of the surfaces were detected by attenuated total reflection Fourier Transform infrared–Raman spectroscopy (ATR-FTIR, EQUINOX 55, Bruker Co., Germany).

Results and discussion

TEM images of the three types of colloid particles used in this study are shown in Fig. 1. The diameters of PS are about 200 and 500 nm, and the diameter of the silica particles is about 50 nm. Aluminium foils coated by a pure silica sol–gel and silica-PS sol–gels containing PS of different sizes were researched, and uncoated aluminium foil was also used for comparison. The 2-dimensional (D) and 3-D nano/microstructure of the surface of the coated aluminium foil was studied by AFM (Fig. 2). From the 2-D images (Fig. 2(a)–(c)), the coating prepared from the pure silica sol–gel (Fig. 2(a)) is composed of dense silica particles, and the size of silica particles is ∼50 nm which is coincident with the TEM observation (Fig. 1(c)). The other two coatings (Fig. 2(b) and (c)) prepared from silica-PS sol–gels are porous, because there are many holes distributed on the surfaces. These holes may be created by the volatilization and decomposition of PS during the heat treatment. From the 3-D images (Fig. 2(d)–(f)), the roughness of each surface can be estimated. The coating prepared from the pure silica sol–gel (Fig. 2(d)) is so smooth that the 50 nm particles can be detected clearly in the 3-D images. However, for the coatings prepared from silica-PS sol–gels (Fig. 2(e) and (f)), the surface structure is very rough, and the silica particles cannot be detected by AFM at the same magnification. Such rough surfaces are composed of many pinnacles each of which has a hole on its top which makes it look like a volcano. The coating prepared from 500 nm PS is obviously rougher than the coating prepared from 200 nm PS.

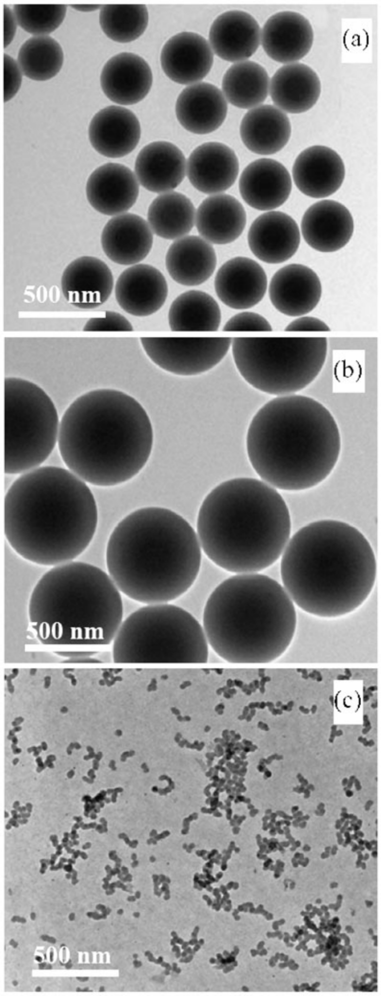

Fig. 1 TEM images: (a) 200 nm PS, (b) 500 nm PS, and (c) 50 nm silica particles.

The water repellence of the coated aluminium substrate can be estimated directly from the shape of a water droplet placed on the surface. The optical images of a water droplet on different surfaces are shown in Fig. 3. When the aluminium foil was modified directly by FAS, its CA was only 110°, and the shape of the water droplet was a hemisphere (Fig. 3(a)). When the aluminium substrate was coated by a silica coating, the CA increased from 110° to 145° (Fig. 3(b)), indicating the significant effect of the silica coating on improving the CA. For further CA improvement, PS of two sizes were used as a removable template. The aluminium substrates coated from the silica-PS sol–gel containing 200 and 500 nm PS show superhydrophobicity with CAs larger than 150° (Fig. 3(c) and (d)). Particularly, for the coating prepared from silica-PS sol–gel containing 500 nm PS, a water droplet with a volume less than 4 μL cannot be placed onto the foil. The CA of a water droplet of 4 μL can reach 160 ± 2° (Fig. 3d). The weight of a 4 μL water droplet is so large that the negative effect of its gravity cannot be neglected. As a result, the measured CA is actually lower than the true CA. The water droplet looks like a ball, and maintains this morphology even when its volume increases from 4 μL (Fig. 3(d)) to 15 μL (Fig. 3(e)). Such observation shows the excellent water repellence of the prepared coatings.

FAS was used to lower the surface free energy of the coated substrate. The CA of water on the aluminium substrate coated from the silica-PS sol–gel was close to 0° before FAS modification, showing a superhydrophilic nature of the unmodified silica coating. However, after FAS modification, the CA increased to >150°. Particularly, for the sample coated from the sol–gel containing 500 nm PS, the CA reached 160°, indicating that there is a significant effect of FAS modification on the SH property. The chemical compositions of the surfaces of the aluminium foils with or without a SH coating were studied by ATR-FTIR and typical results are shown in Fig. 4. On the surface of the coated SH foil, a strong absorption peak in the 1000–1200 $\mathrm{cm^{-1}}$ region was detected, whereas on the

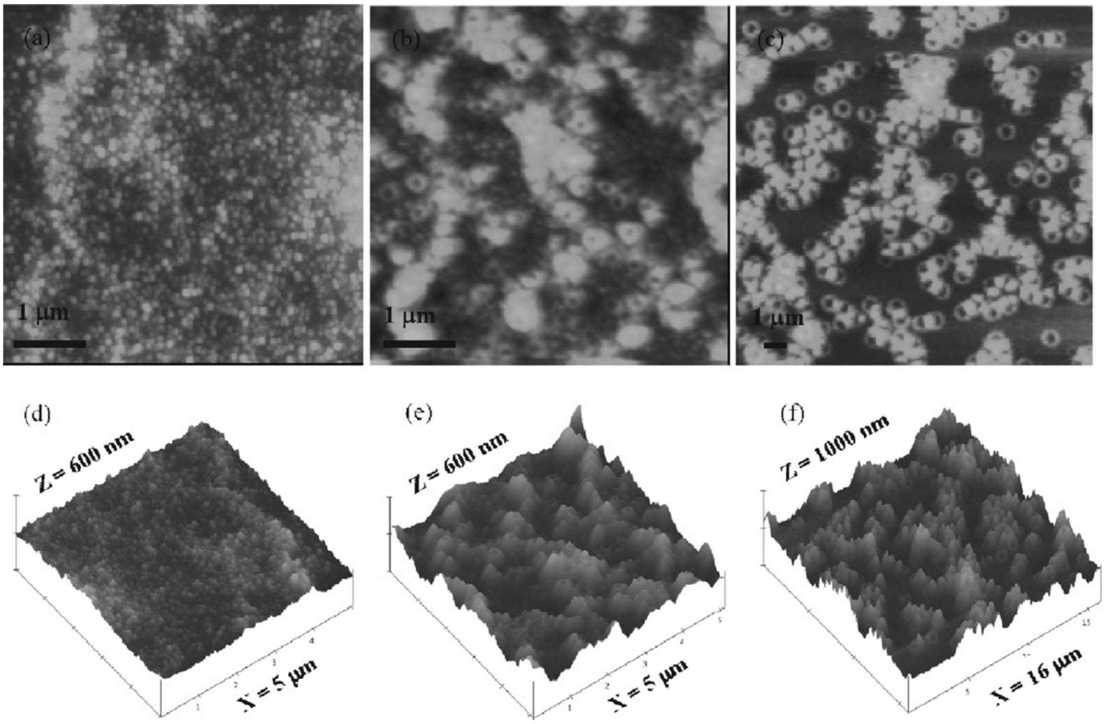

Fig. 2 AFM images of coatings prepared from sol–gel containing: (a) and (d) no PS, (b) and (e) 200 nm PS, (c) and (f) 500 nm PS; (a)–(c) correspond to the 2-D morphologies of the coatings, whereas (d)–(f) are the 3-D morphologies of the coatings.

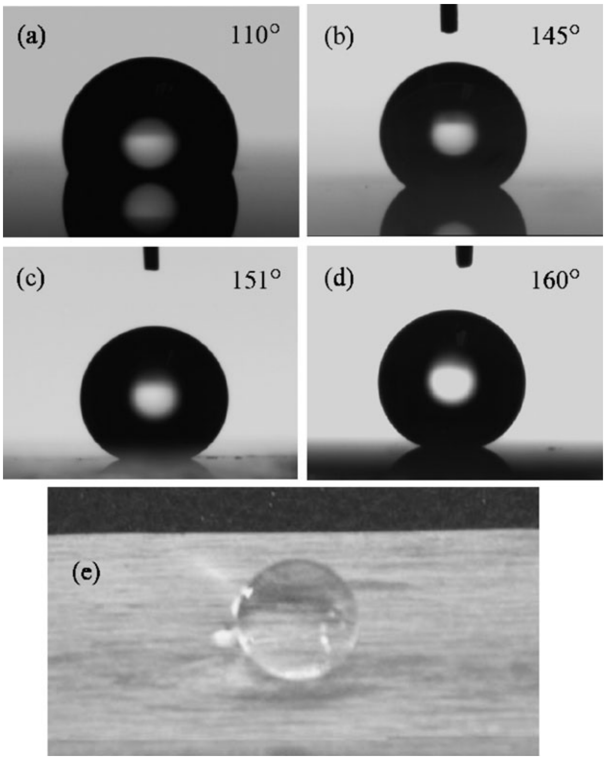

Fig. 3 Optical images of a 4 µL water droplet (a)–(d) on FAS-modified aluminium substrates with different coatings. (a) Uncoated aluminium, (b) coated from silica sol–gel containing no PS, (c) coated from silica-PS sol–gel containing 200 nm PS, (d) coated from silica-PS sol–gel containing 500 nm PS. (e) As for (d) but with a 15 µL water droplet of 15 µL.

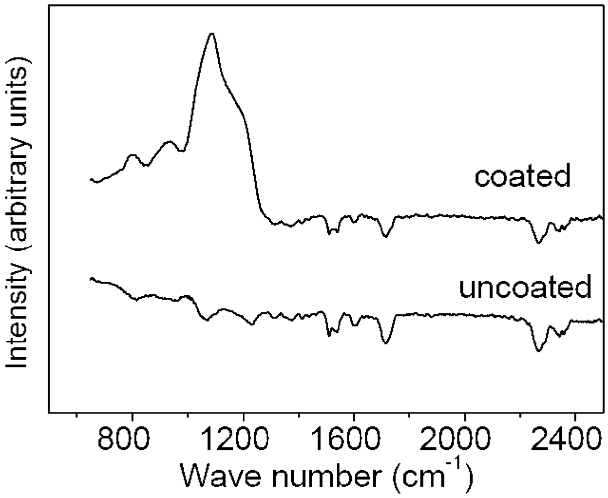

Fig. 4 ATR-FTIR spectra of aluminium foils with or without a SH coating.

uncoated aluminium foil no obvious absorption peaks were found in the same region. The absorption peak in the 1000–1200 cm^{-1} region is believed to be originated from –CF_2– and –CF– groups in FAS, indicating that the FAS has been successfully introduced on the SH coating.

The chemical composition and the nano/micro-structure of the coated surface are the two main factors determining the SH property. In the studied case, all the surfaces are covered by monomolecular FAS with the same treatment, and the chemical compositions are the same according to the results of ATR-FTIR. Thus, the CA of the prepared surface is mainly determined by the nano/micro-structure of the surface. In other words, the CA increases with increasing the roughness of a surface when the chemical composition is kept the same. This result is consistent with the Wenzel and Cassie-Baxter models, which are used for explaining SH phenomena.

Although both of the static CAs of the two coatings prepared from sol–gels containing 200 and 500 nm PS exceeds 150°, the adhesive forces between the coatings and water droplet are very different. The coating from 200 nm PS shows strong adhesion with the water droplet, and the water droplet cannot slide off the coated aluminium substrate by gravity even when the substrate is placed vertically as shown in Fig. 5(a). However, for the coating from 500 nm PS, the adhesion is very weak. As a result, the water droplet can roll off the slightly tilted (less than 5°) substrate easily (Fig. 5(b) and (c)).

The adhesion mainly comes from the van der Waals force produced by the liquid–solid interface between the water droplet and the coated substrate.[26] Thus, the adhesion is proportional to the area of the liquid–solid interface, which can be affected by the surface roughness, according to the Wenzel and Cassie-Baxter models.[27,28] In Wenzel's model, the roughness can increase the area of the liquid–solid interface between the water droplet and the coated substrate, and the adhesion is large. However, in the Cassie-Baxter model, because of the high roughness and specific geometry,[29] the surface can still trap a large amount of air when a water droplet is placed on such a surface. As a result, the interface between the water droplet and the substrate consists of liquid–solid and liquid–gas interfaces. Since the area of the liquid–solid interface is very small, a water droplet is unstable on such surface.

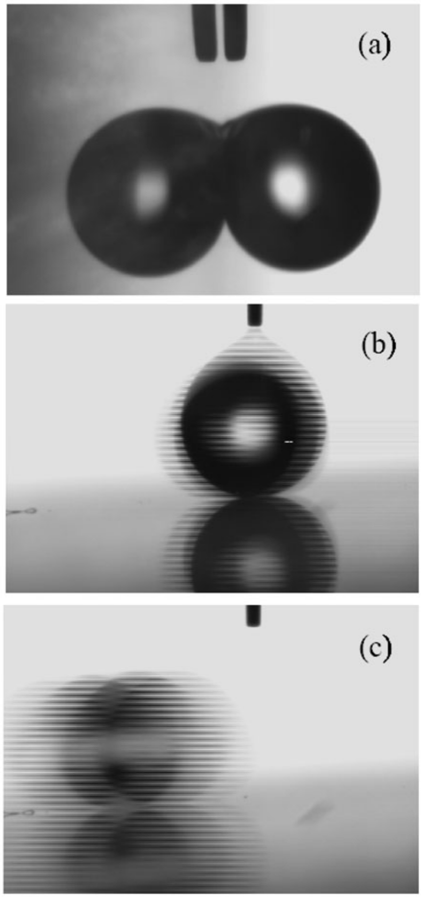

Fig. 5 (a) A water droplet sticking on the vertically oriented SH surface prepared from a sol–gel containing 200 nm PS; (b, c) A water droplet rolling off a slightly tilted SH surface prepared from a sol–gel containing 500 nm PS.

For the coating prepared from the sol–gel containing 200 nm PS, although the CA reaches 150°, the surface is not very rough and can trap only a small amount of air. When a water droplet is placed onto the surface, most of the air is removed and the area of the liquid–solid interface is large. As described by Wenzel's model, the large area of the liquid–solid interface creates strong adhesion with a water droplet. Thus, the water droplet can stick on the substrate even tilted vertically.

For the coating prepared from the sol–gel containing 500 nm PS, the surface is rougher (Fig. 2(d)–(f)) and can trap more air than the coating prepared from 200 nm PS. When a water droplet is placed on it, a large amount of air can be trapped within the pores of the contact area. This reduces the area of the liquid–solid interface to a very low level as described by Cassie-Baxter's model. As a result, the CA is as high as 160°, and the adhesion between the water droplet and substrate decreases down to a negligible level, and the water droplet can roll off very easily.

The chemical stability of the prepared SH surface had been researched. The CA did not decrease after a year of exposure in air. Additionally, the CA of a water droplet with pH from 2 to 12 on an aluminium substrate prepared from a sol–gel containing 500 nm PS was measured. The results are shown in Fig. 6. The CA is almost unchanged in a wide range of pH values. Such observation indicates that the coated SH aluminium substrate has a good stability. This is due to the intrinsic chemical stability of FAS and silica particles.

To test its corrosion resistance, the coated aluminium substrate was immersed into a solution of acetic acid with a pH value of 3 for 5 h. After this treatment, the CA was still as high as 160°, indicating the stability of the chemical

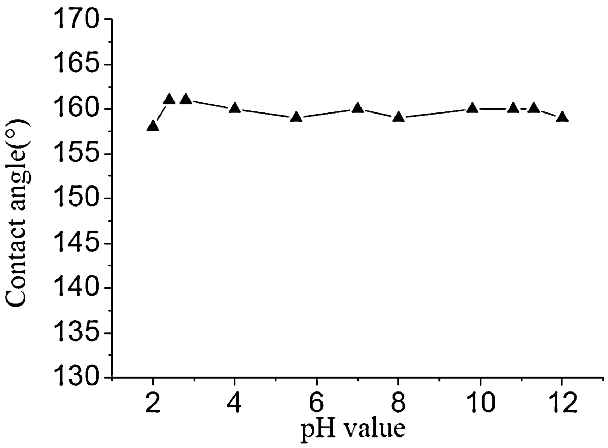

Fig. 6 Contact angles of water droplets with different pH values on the prepared superhydrophobic surface.

composition and nano/micro structure of the surface. When the coated aluminium foil is immersed into the acid solution, the air trapped in the SH surface can prevent the direct contact between the acid solution and the aluminium foil. Since the SH coating itself has an intrinsic chemical stability and cannot be corroded by the acid solution, the aluminium foil can be protected from corrosion by the SH coating.

Conclusions

In conclusion, we have prepared SH coatings on aluminium foil by a simple sol–gel method. PS is used as a removable template. The effects of the size of PS on the surface structure and thus its superhydrophobicity have been researched. When using 200 nm PS, the prepared coating shows a high static CA larger than 150°. Because of a large adhesion, a water droplet can be pinned on the substrate even tilted vertically. Such a coating may be useful for some intelligent microfluidic devices. However, when using 500 nm PS, the prepared coating has a CA as high as 160°, and the water droplet can roll off the substrate easily. In addition, such a coating also possesses good chemical stability. Its superhydrophobicity can be maintained after a year of exposure in air for water droplets with a wide range of pH values (from 2–12). More importantly, such a coating can protect the aluminium foil from corrosion during the immersion in an acid solution with a pH value of 3 for 5 h. These properties are favorable for the potential applications of the coated aluminium foil in air-conditioning facilities or other rigorous circumstances.

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