Facile Fabrication of Polysiloxane Nanorods on Magnesium Surface in the Presence of 1,6-diphosphono-hexane to Obtain a Superhydrophobic Surface

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Superhydrophobic surfaces have been the focus of both industry and academic research. The high water repellency exhibited by these surfaces is based on a natural phenomenon (i.e. Lotus effect).[1-3] Superhydrophobicity is explained by the Wenzel and Cassie-Baxter model.[4,5] According to this model, the air trapped in micro-/nano-scale rough surfaces is a key factor in making these surfaces superhydrophobic. The trapped air and the micro-/nano-scale rough surface act to suspend the water droplet on the tops of the surface microstructure. In nature, there are many examples of plants and animals utilizing superhydrophobicity for various purposes.[6-10] There are two factors that determine the superhydrophobicity of a surface. The first one is the chemical composition on the surface, which for superhydrophobicity, must have low surface energy. The second factor is the geometrical structure of the surface.

Surface roughness is a key factor controlling wettability because it determines the contact area between a water droplet and the surface.[11,12] One of the criteria for superhydrophobicity is that the water contact angle of the surface should be more than $150°$. A water droplet on even a slightly tilting superhydrophobic surface will not remain on it but will roll off. This property can be exploited to remove contaminants on a superhydrophobic surface using water droplets. The lotus leaf possesses this self-cleaning property, which originates from the wax-covered microstructures on its surface. This self-cleaning effect has been exploited for various applications such as for developing water repellency coatings, preventing snow sticking, and enhancing the lubricity of micro-fluidic devices.[13-15] However, the fabrication of superhydrophobic surfaces requires the preparation of micro-/nano-scale rough surfaces, and thus many methods have been developed to fabricate such surfaces; these methods include metal atom deposition, the sol-gel method, and etching process.[16-21]

However, these methods are generally complex and require the use of expensive devices. Therefore, a simple and inexpensive approach for obtaining industrially feasible superhydrophobic surface is required.

Polysiloxane is a well-known hybrid organic-inorganic material, and it has been studied extensively. Polysiloxane is prepared by the hydrolysis and condensation of alkyl triethoxysilanes. A series of reactions are carried out to finally produce oligomers and polymers. There are many complex reactions that produce many different polysiloxanes. Mabry *et al.* prepared the fluorinated polyhedral oligomeric silsesquinoxane using one-pot synthetic method.[22] The surface that was coated with this fluorinated polyhedral compound exhibited hydrophobic property whose effectiveness was dependent on the length of the fluoroalkyl chain.

Fluorinated alkyl silane and alkyl silane have been used to coat micro/nano-scale rough surfaces to obtain a superhydrophobic surface.[23-25] This coating layer is transparent. Generally, the alkyl silane derivative used as the coating layer is a flexible amorphous polysiloxane or a transparent self-assembled monolayer. In 1997, Parikh *et al.* obtained the crystalline structure of polymerized octadesylsiloxane (PODS).[26] Li *et al.* obtained a superhydrophobic surface with liquid *n*-octadecyl trichlorosilane. A nanosheet of PODS was obtained by coating a glass surface with liquid PODS and then dipping the glass surface in an organic solvent. The nanosheet was obtained by the forming of a self-assembled structure that then underwent polycondensation.[27,28]

In the present study, we have demonstrated the facile synthesis of nano-rode structures of polysiloxane on a metal surface achieved by simply dipping Mg piece in a mixture solution of alkyltriethoxysilane and 1,6-diphosphonohexane. The prepared rough surface of the Mg piece was coated with a solution of stearic acid in alcohol to obtain superhydrophobic surface.

Experimental

Instrumentation. The water contact angles of the modified Mg surface were measured using a contact angle analyzer (Phoenix 300, Surface Electro Optics) at ambient temperature. The morphology of the surface was observed using a field emission scanning electron microscope (FE-SEM, Hitachi S4300, Hitachi Inc.). The X-ray photon electron spectroscopy (XPS) spectrum of the surface was obtained using a spectrometer (MultiLab 2000, Thermo VG Scientific). Another spectrometer (Travel IR, Sens IR technologies) was used to obtain the external Fourier transform infrared (FTIR) spectra. Heptadecafluoro-1,1,2,2-tetrahydrodecyl trimethoxysilane (HFTHTMS) was purchased from Gelest Inc. (U.S.A). Mg flakes with a size of 1.0 cm × 1.9 cm × 0.01 cm were cleaned ultra-sonically with 5% HCl for

2 min, and then with distilled water and ethanol.

General Procedure for the Preparation of the Rough Surface and the Coating. a) To a solution of 1-{3-(tri-ethoxysilyl)}propyl-3-hexyl urea[29] (0.08 g, 0.2 mmol) in ethanol was added 1.6-diphosphono-hexane (0.043 g, 0.1 mmol). After continuous stirring for 1 h, an ultra-sonically cleaned Mg piece was dipped in this solution for 5-10 min at room temperature. The Mg samples were dried at 80° in an oven and then cooled at room temperature. Then, they were dipped in an ethanol solution of 2% stearic acid for 5 min and dried at room temperature.

b) Another coating solution was prepared from HFTHTMS (0.08 g, 0.14 mmol), ethanol (10 mL), and 1,6-diphosphono-hexane (0.043 g, 0.1 mmol) according to the general procedure.

Results and Discussion

A Mg piece was dipped in a solution of hexyl urea silane and 1,6-diphosphono-hexane in ethanol for 5 min. Well-arranged nano-scale structures, nanorods, were observed on the surface of Mg alloy by FE-SEM. The diameter of these nano-rods was 0.12-0.15 μm and their length was 1.6-2 μm. This well-arranged nano-rod structure on the Mg surface was expected to be superhydrophobic. However, the water contact angle of the coated surface was 100°, which is still short of satisfying the condition for superhydrophobicity.

Fluorinated alkyl silane derivatives are popular coating materials to obtain a superhydrophobic surface. Therefore, HFTHTMS was used as a fluorinated alkyl silane derivative for fabricating nano-rods on the Mg surface. The resultant nano structure appeared very similar to that obtained with hexyl urea silane. We expected that the water contact angle of the surface fabricated with fluorinated alkyl silane and phosphate derivatives would be superhydrophobic. However, in this case the water contact angle of the surface was 103° (Fig. 1).

Generally, *n*-alkyl triethoxysilane or fluorinated alkyltriethoxysilane is hydrolyzed and polymerized to produce a self-assembled alkyl silane coating having a low surface energy. A surface is fully grafted by SAM which results in CH_3- and CH_2- (or CF_3 and CF_2- in fluorinated alkyl silane) groups being exposed, thus making the surface superhydrophobic. Our results showed that neither the fluorinated alkyl silane nor the alkyl urea silane formed self-assembled layers on the nano-rod structure. We suppose that diphosphono-hexane which was used in the solution synthesis may have contributed to the less hydrophobic character of the nano-rod structure on the Mg surface.

In solution synthesis, an organic molecule is commonly used to control the size and shape of the inorganic crystal. When a coating solution is prepared without using 1,6-diphosphono-hexane, the resultant coated surface shows a morphology resembling balls with a diameter of about 1.7 μm (shown Fig. 2). In previous studies, liquid octadecyltrichlorosilane (OTS) was used directly for coating material; glass slides coated with OTS were immersed in acetone,[27]
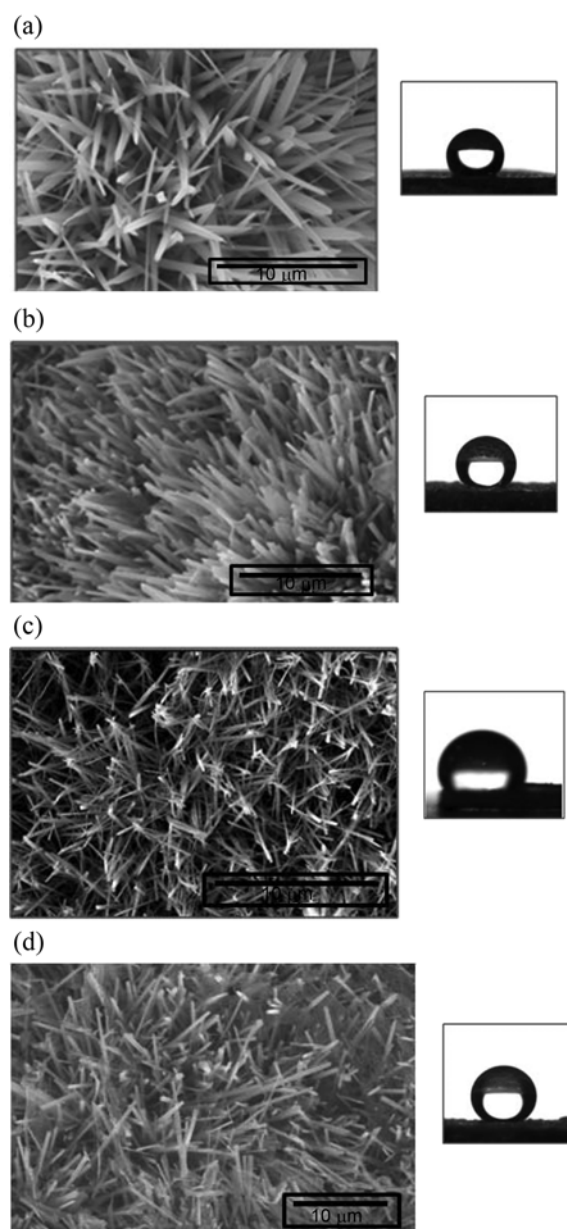

Figure 1. SAM images of polysiloxane nano-rods with different substrates and the corresponding images of water drops on the coatings (a) hexyl urea silane (b) modified with solution of 2% stearic acid in ethanol (c) HFTHTMS (d) modified with solution of 2% stearic acid in ethanol.

and the resultant polymerized *n*-octadecylsiloxane (PODS) formed a superhydrophobic nanosheet. The white coating layer is fragile and easily removed.[28]

In the current experiment, nano-rods of polysiloxane were formed by adding 1,6-diphosphono-hexane. 1,6-Diphosphono-hexane has an influence on the growth of polysiloxane. Moreover, we decided that the nano-rod coated surface could be modified by stearic acid to obtain a superhydrophobic surface. After such a modification, we found that the contact angle of the surface had increased (Fig. 1).

In order to investigate the effect of length of the nano-rods on the contact angle of the surface, the dipping time was varied. When the Mg piece was dipped for 5 min, and for
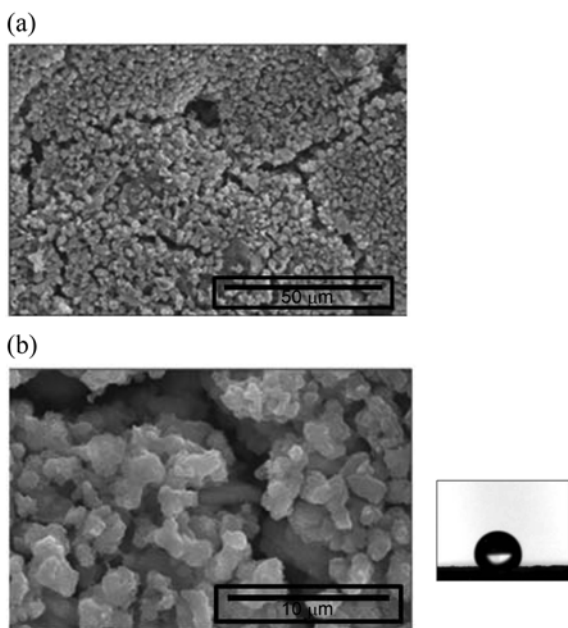
Figure 2. SEM images of Mg surface coated with the solution of hexyl urea silane without 1,6-diphosphono-hexane. Water droplet on the surface unmodified with 2% stearic acid.
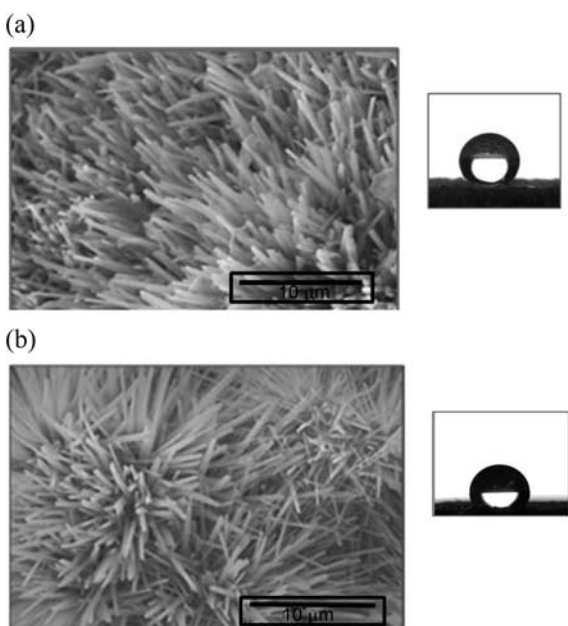

Figure 3. SEM images of polysiloxane nano-rods on Mg surface at different dipping times and the corresponding photograph of water droplets on polysiloxane nano-rods on Mg surface modified with 2% stearic acid. (a) 5 min and (b) 5 h.

Figure 4. IR spectrum of a polysiloxane nano-rods coated Mg surface followed by coating with solution of 2% stearic acid in ethanol.

Figure 5. XPS spectrum of a polysiloxane nano-rods coating followed by coating with solution of 2% stearic acid in ethanol.

5 h, the lengths of nano-rods grown were 2 μm and 10 μm, respectively. The corresponding water contact angles were around 150° and 90°, respectively (Fig. 3). When the dipping time was 5 min, the nano-rods covered a large area of the Mg substrate uniformly and compactly. The change of length produced by increasing the dipping time led to a change in the contact angle. However, at an increased dipping time from 5 min to 5 h, the nano-rods had grown too long, as shown in Figure 2(b) to support a water droplet on the surface.
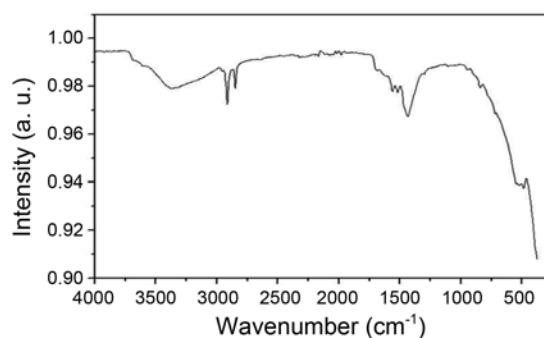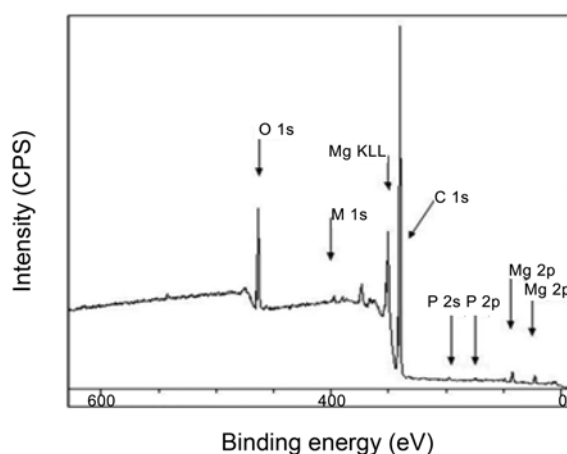
The IR spectrum of the modified Mg surface is shown in Figure 4. The peaks at 2916 and 2850 cm^{-1} correspond to the asymmetric and symmetric stretching of the CH$_2$ groups, respectively. An intermolecular hydrogen bond appears as a very broad band with maximum absorption at approximately 3340 cm^{-1} and the peak at 1428 cm^{-1} is ascribed to the vibration of C-O group. The typical carbonyl band of stearic acid is not observed at 1710 cm^{-1}.

To confirm the presence of phosphate groups on the coated surface of the Mg piece, an XPS spectrum was obtained. Figure 5 shows the XPS spectrum of the modified surface of Mg alloy. The phosphate signals found were P$_{2s}$ at 195 eV and P$_{2p}$ at 134 eV.[30] The absorbance of C, O, and P demonstrates that the magnesium surface was covered by polysiloxane, phosphate material, and stearic acid.

We attempted to collect the solid material of the coating using a surgical razor, however, we failed. As a result, we were unable to carry out spectroscopy analyses (NMR and X-ray crystallography) of the coating.

Figure 6 shows the relationship between the pH and the water contact angle of the modified surface of the Mg alloy. The water contact angel of the modified surface showed no
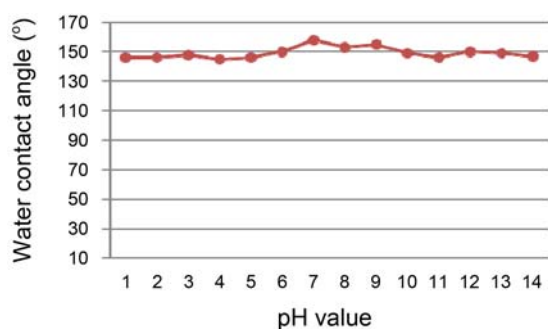
Figure 6. Relationship between pH and water contact angle on superhydrophobic surfaces. The contact angles were measured by depositing a 5 uL water droplet onto the surface.

obvious variation when the pH was increased from 1 to 14. That is, the superhydrophobicity of the surface was stable over a broad range of pH values. These results showed that the pH of the aqueous solution had little effect on the superhydrophobicity of the coated surface.

Conclusion

In conclusion, polysiloxane nano-rods were fabricated on a Mg surface by dipping a Mg piece in a mixture solution of alkyl triethoxysilane (or fluorinated alkyl triethoxysilane) and 1,6-diphosphono-hexane in ethanol. The nano-rod surface was coated with stearic acid to realize superhydrophobicity. This new method for producing superhydrophobic nano-rod structured surfaces can be useful for application in various fields. Investigations of the morphology of the surface obtained by this method showed that the properties of nano rods and nanoscale rough surfaces were dependent on the immersion time of the surface in the mixture solution of alkyl triethoxysilane and 1,6-diphosphono-hexane. These results show that very high crystalline polysiloxane can be easily and quickly synthesized from alkyl urea silane (or HFTHTMS) and 1,6-diphosphono-hexane. Phosphate derivative functions as a structure modifier, and thus it is very useful for applying structural typologies. In future work, we will focus on the investigation of the growing mechanism of the nano-rod structure of polysiloxane in the presence phosphate derivatives.

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