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One-Step Solution Immersion Process to Fabricate Superhydrophobic Surfaces on Light Alloys

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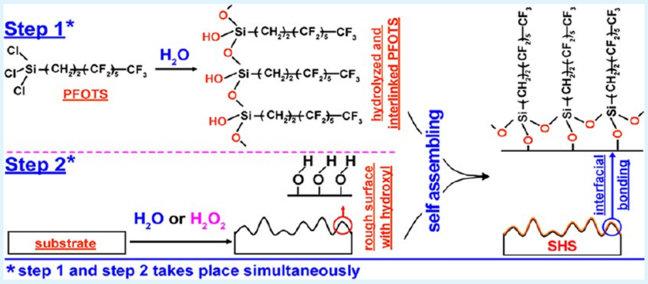
Supporting Information

ABSTRACT: A simple and universal one-step process bas been developed to render light alloys (including AZ91D Mg alloy, 5083 Al alloy, and TC4 Ti alloy) superhydrophobic by immersing the substrates in a solution containing low-surface-energy molecules of 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS, 20 μL), ethanol (10 mL), and H_2O (10 mL for Al and Mg alloy)/H_2O_2 (15%, 10 mL for Ti alloy). Field-emission scanning electron microscopy, X-ray photoelectron spectroscopy, and water contact angle measurements have been performed to characterize the morphological features, chemical composition, and wettability of the surfaces, respectively. The results indicate that the treated light alloys are rough-structured and covered by PFOTS molecules; consequently, the surfaces show static contact angles higher than 150° and sliding angles lower than 10°. This research reveals that it is feasible to fabricate superhydrophobic surfaces (SHS) easily and effectively without involving the traditional two-step processes. Moreover, this one-step process may find potential application in the field of industrial preparation of SHS because of its simplicity and universality.



KEYWORDS: *superhydrophobicity, light alloys, one-step process*

1. INTRODUCTION

In recent years, superhydrophobic surfaces (SHS) with a water static contact angle (SCA) above 150° and sliding angle (SA) below 10° have attracted considerable interest in both fundamental research (such as the thermodynamic analysis on wetting behaviors of SHS[1,2]) and practical potential applications (such as self-cleaning, corrosion resistance, anti-icing, etc.[3−9]). The aim of these fundamental researches is to reveal the origin of superhydrophobicity and further set guidelines for the fabrication of SHS; meanwhile, the realization of these potential applications often relies on fabrication of SHS by a simple and feasible way. So, it can be seen that the fabrication of SHS is a key factor influencing the development of SHS.

Heretofore, various SHS have been fabricated. The most typical method adopted is first to create rough structures on different substrates (such as metal,[10−13] glass,[14−16] ceramic,[17,18] and polymer[19]) and subsequently passivated by low-surface-energy molecules (such as fluoroalkyl-silane,[10−12,14,15,17,18] fluoroalkyl mercaptan,[13] poly(alkyl siloxane),[16] hydrophobic silica,[19] etc). This is a so-called two-step process, which is superior for its universality and inferior for its complex operations. To overcome the inherent disadvantage (i.e., complex operations), researchers have developed several solution-immersion one-step processes, in which both the creation of rough structures and the lowering of the surface energy take place simultaneously in one single step. For instance, Jiang et al.[20] and Hong et al.[21] have fabricated SHS on copper plate by immersing the substrate in an ethanol solution of myristic acid. Under this situation, myristic acid is supposed to react with copper ions to form copper carboxylate $\{Cu[CH_3(CH_2)_{12}COO]_2\}$, which is low-surface-enegied and flower-like structured. Saleema et al[22,23] (ethanol−HCl−myristic acid) and Zhang et al.[24] [H_2O−NaOH−FAS-17 (1H,1H,2H,2H-perfluorodecyltrichlorosilane)] have proposed multisolute solutions to fabricate SHS on Al alloy by one-step process, in which HCl or NaOH is supposed to etch the substrate and low-surface-energy molecule of myristic acid or FAS-17 is assembled thereon. Such few solution-immersion one-step examples are impressive for its easy operation; however, these methods are confined to certain substrates (such as copper and aluminum alloy) and it is difficult to be popularized.

Herein, a novel one-step superhydrophobization strategy suitable for light alloys of Al, Mg and Ti has been developed, which is inspired by the composition of above-mentioned multisolute solutions (ethanol−HCl−myristic acid or H_2O−NaOH−FAS-17) and our most recent work (in which H_2O or H_2O_2 is adopted as the etcher to roughen the light alloys).[25]

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The detailed procedure is to immerse the substrates in a solution containing ethanol, H_2O (for Al and Mg alloys)/H_2O_2 (for Ti alloys), and PFOTS molecules. The role of ethanol is to dissolve the low-surface-energy molecules of PFOTS, which is supposed to be assembled on the rough structures generated by the oxidation effect of H_2O or H_2O_2.

Compared with previous pioneer researches, this strategy is quite impressive for its relatively wider applicability to light alloys of Al, Mg and Ti; moreover, the chemical etcher used is H_2O or dilute H_2O_2, which has no or low impact on environment as compared with HCl or NaOH. Based on these features, it is hoped that this strategy will accelerate the practical production of SHS on light alloys by a solution-immersion one-step process.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Mg alloy (AZ91D), Al alloy (5083), Ti alloy (TC4) was obtained from Northwest Institute of Nonferrous Metal Company, China. 1H, 1H, 2H, 2H - perfluorooctyltrichlorosilane (PFOTS) was purchased from Sigma-Aldrich. Other reagents are analytical grade and used as received. Ultrapure water with a resistivity greater than 18.0 MΩ cm was used.

2.2. Preparation of SHS. To get rid of surface contamination, we ground the light alloys with abrasive paper (600 Cw and 1200 Cw), and subsequently ultrasonicated in acetone, ethanol as well as ultrapure water for 10 min, respectively. The alloys were then introduced into solutions containing ethanol (10 mL), PFOTS (20 μL), and H_2O (10 mL for Mg and Al alloys) or H_2O_2 (15%, 10 mL for Ti alloy) at 60 °C for 6 h in a sealed vessel. After this, the samples were taken out and ultrasonically cleaned in ultrapure water for 2 min and dried with N_2 gas.

2.3. Characterizations. An optical contact angle meter (Easydrop, Krüss, Germany) with a computer-controlled liquid dispensing system and a motorized tilting stage was used to measure water static contact angle (SCA) and sliding angle (SA) at ambient temperature (25 °C) with 7 μL of ultrapure water as probe liquid.

The morphological microstructures were observed on filed emission scanning electron microscope (FESEM, Nova NanoSEM, FEI, USA) under vacuum environment and the samples were presputtered with a thin palladium/gold film. We studied the chemical compositions of the samples by X-ray photoelectron spectroscopy (XPS, Physical Electronics, PHI-5702, USA). The measurements were performed using a monochromated Al−Kα irradiation and the chamber pressure was about 3×10^{-8} Torr under testing condition. The binding energy of adventitious carbon (C1s: 284.8 eV) was used as a basic reference.

3. RESULTS AND DISCUSSION

It is well-known that superhydrophobicity is determined by two important parameters, namely, hybrid micro/nanosurface structures and low surface energy. Herein, these two prerequisites are supposed to be realized in a single one-step process. To confirm such supposition, the samples after treatment by $H_2O/H_2O_2-C_2H_5OH$-PFOTS are characterized by FESEM (Figure 1) and XPS (Figure 2). From Figure 1, it is observed that the treated light alloys exhibit different rough surface structures. Specifically, for Al alloy, the surface is densely covered with petals, the thickness of which is several ten nanometers and the length of which is several micrometers. The disordered arrangement of these petals leads to a rough structures. For Mg alloy, the surface is covered by microflowers; under larger magnification, it is obvious that the microflowers are made up of nanosheets. For Ti alloy, the surface is cracked to form microislands and some agglomerated particles deposited thereon; under larger magnification, it can be seen that the surface of the such particles is uneven with nanonadel.

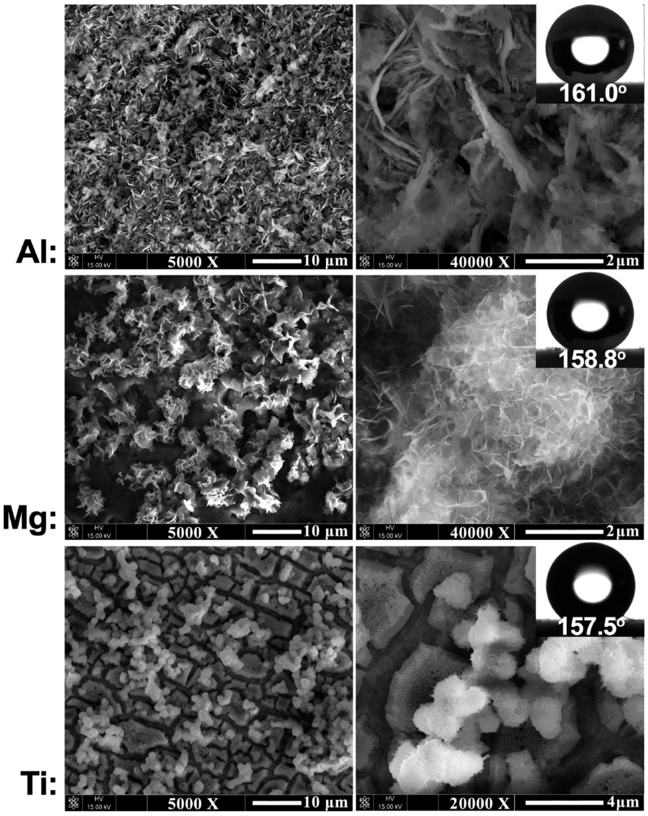

Figure 1. FESEM images for different samples treated by $H_2O/H_2O_2-C_2H_5OH$-PFOTS. SCAs are shown in the inset images and SAs for the samples from up to down are 8, 5, and 6°, respectively.

So, it can be concluded that such a one step process is effective in fabricating hybrid micro/nanosurface structures on light alloys.

XPS was performed to investigate the surface chemistry of samples treated by $H_2O/H_2O_2-C_2H_5OH$-PFOTS. Besides the signals originated from the substrate (such as Al, Mg, and Zn signals for Al alloy; Mg and Zn signals for Mg alloy; Ti signal for Ti alloy), other signals in the survey spectra (such as F 1s, Si 2p, C 1s, and O 1s, see the Supporting Information) can be attributed to the adsorbed PFOTS molecules. Specifically, F 1s (see the Supporting Information) and Si 2p (Figure 2) peaks are direct and obvious evidence for the adsorption of PFOTS. The high resolution C 1s core level spectra (Figure 2), resolved into four components, namely, $-CF_3$, $-CF_2$, $-{}^*CH_2-CF_2$, and $-CH_2-CH_2-$, can also be regarded as another evidence.[22] The amount ratio of $-CF_2$ and $-CF_3$ from the spectra, which is 4.8: 1 (Al), 5.5: 1 (Mg), or 5.0: 1 (Ti), is close to the theoretical value of PFOTS (i.e., 5: 1), indicating that the low-surface-energy CF_3 and CF_2 components comprise the outermost surface.

After being treated by $H_2O/H_2O_2-C_2H_5OH$-PFOTS, the water droplet on the surface shows a nonwetting state, just as shown in the right insets of Figure 1. The average SCA/SA for Al, Mg, and Ti alloys are 162.5 ± 2.0°/7 ± 2°, 160.2 ± 2.5°/5 ± 1°, and 158.5 ± 1.5°/5 ± 1°, respectively; indicating that SHS are fabricated successfully. Such superhydrophobicty could be explained by Cassie wetting model[26]

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

which is generally valid for heterogeneous interface composed of air/liquid and solid/liquid. Here, θ_c is the SCA of the so-

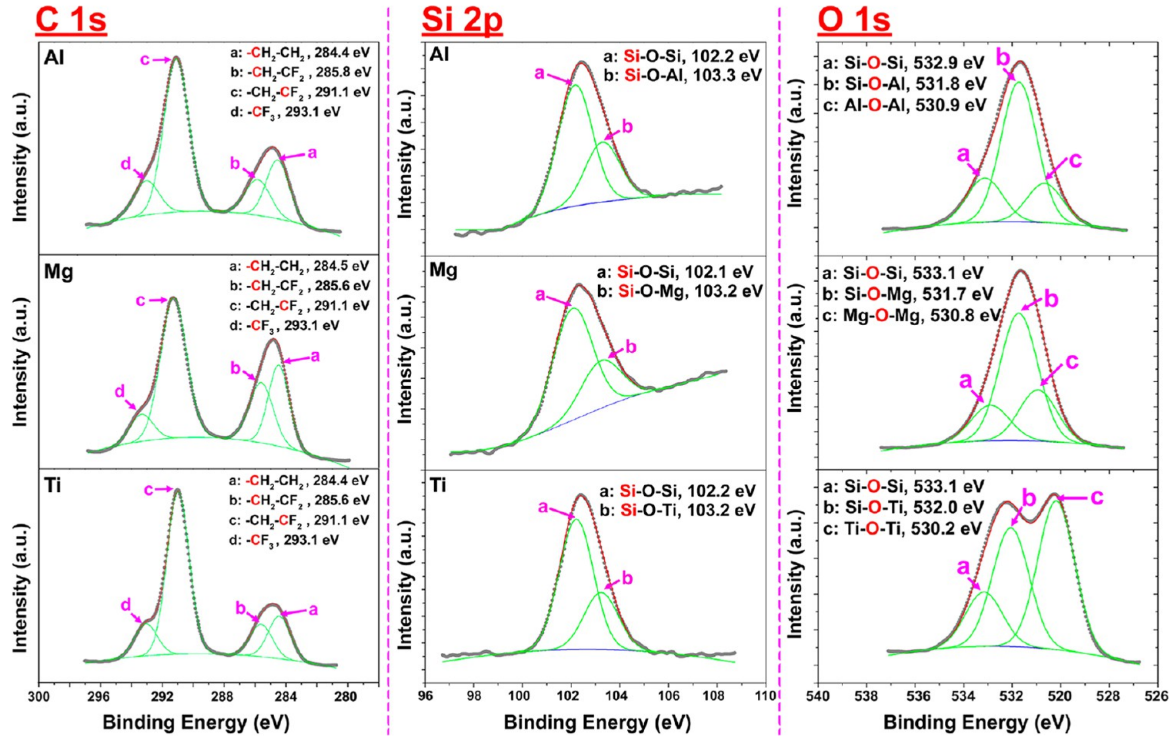

Figure 2. XPS for different samples treated by $H_2O/H_2O_2-C_2H_5OH$-PFOTS.

fabricated SHS; θ is the contact angle of the smooth surface modified with PFOTS (measured to be 110 ± 2.0° on a smooth Si surface); and f_1 is the fraction of solid/liquid interface and f_2 the air/liquid interface ($f_1 + f_2 = 1$). This equation predicts that increasing the fraction of air/liquid interface (f_2) should increase the SCA (θ_c). According to the equation, and $\theta_c = 160°$ (a typical SCA for the so-fabricated sample)/$\theta = 110°$, f_2 is estimated to be 0.91. This means that air occupies about 91% of the contact area between the water droplet and the SHS, which is responsible for the superhydrophobicity of the surface.

As shown in Figure 3a, the wettability of the so-fabricated sample is dependent on the treating temperature and time. Specifically, as temperature increasing, the treating time needed to obtain SHS becomes shorter: under 40 °C, SHS is only obtained on Mg alloy and the critical time is 48 h; under 60 °C, the critical time to obtain SHS on Al/Mg/Ti alloys is 6 h; under 80 °C, the critical time is 4 h. The stability of the so-fabricated SHS (60 °C/6 h, and 80 °C/4 h) or samples with highest SCA (40 °C/48 h) was estimated under ultrasonication for 20 min (Figure 3b). It is observed that, during the ultrasonication process, SCA for Al/Mg is always higher than 150° for 40 °C/48 h, and SCA for Ti decreases sharply from ~143 to ~105°. This suggests that the PFOTS on the Ti is not so stable as that on Al/Mg. This is probably because that, under low temperature of 40 °C, the formation of oxide layer (TiO_2) on the substrate is slow and the surface density of active groups (Ti−OH) is low; consequently, the amount of covalent bonded PFOTS is relatively small. In other words, the physically bonded PFOTS to the substrate is nonignorable, which can be removed by ultrasonication and is responsible for the decreasing in SCA. For samples obtained by 60 °C/6 h and 80 °C/4 h, SCAs are always higher than 150° during the ultrasonication process except for Al/Mg by 80 °C/4 h. This suggests that PFOTS on Al/Mg by 80 °C/4 h is not stable as that on Al/Mg by 60 °C/6 h. This may be explained as follows: in the one-step immersion process, there exists a competition between the reaction of hydrolyzed (or partially hydrolyzed) trichlorosilyl groups with other such groups in solution to form a 3D polymer, and the reaction of such groups with surface M−OH (M = Al, Mg) moieties to form covalent bonded PFOTS.[27] As temperature decreasing, the preference of surface reaction increases. Consequently, at higher temperature of 80 °C, fewer amounts of covalent bonded PFOTS on Al/Mg is expected and the stability is relatively weaker. From above discussions, it can be seen that, to fabricate SHS in a short-term of several hours, temperature should be 60 or 80 °C; however, for 80 °C/4 h, the stability of SHS on Al/Mg under ultrasonication is relatively weaker as compared with 60 °C/6 h. So, 60 °C/6 h is the most optimum condition to fabricate SHS.

The long-term (6 days) stability of SHS fabricated under 60 °C/6 h against contact with NaCl solution (3.5 wt %) was further estimated. Specifically, the so-fabricated SHS was first immersed into NaCl solution for a certain period of time and then the sample was taken out and the static contact angle (SCA)/sliding angle (SA) was monitored. The results (Figure 3c) shows that the surface superhydrophobicity can be retained for 24 h (for Mg, at that point, SCA = 159.5 ± 2.6°, SA = 10.5 ± 1.6°), 60 h (for Ti, at that point, SCA = 157.8 ± 2.2°, SA = 10.1 ± 0.7°), or 72 h (for Al, at that point, SCA = 159.4 ± 2.1°, SA = 10.2 ± 1.5°). In our most recent work,[25] the stability against contact with NaCl solution (3.5 wt %) of control samples, i.e., SHS fabricated by a chemical etching [Al in HCl (3.7 wt %), Mg in HNO_3 (6.8 wt %), Ti in HF (4.0 wt %) for 5 min] and subsequent surface passivation with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES), was also evaluated. It was found that the superhydrophobicity was lost after immersed into the NaCl solution for several hours (<6 h). So, it can be seen that SHS fabricated by such a one-step solution immersion process is much more stable as compared

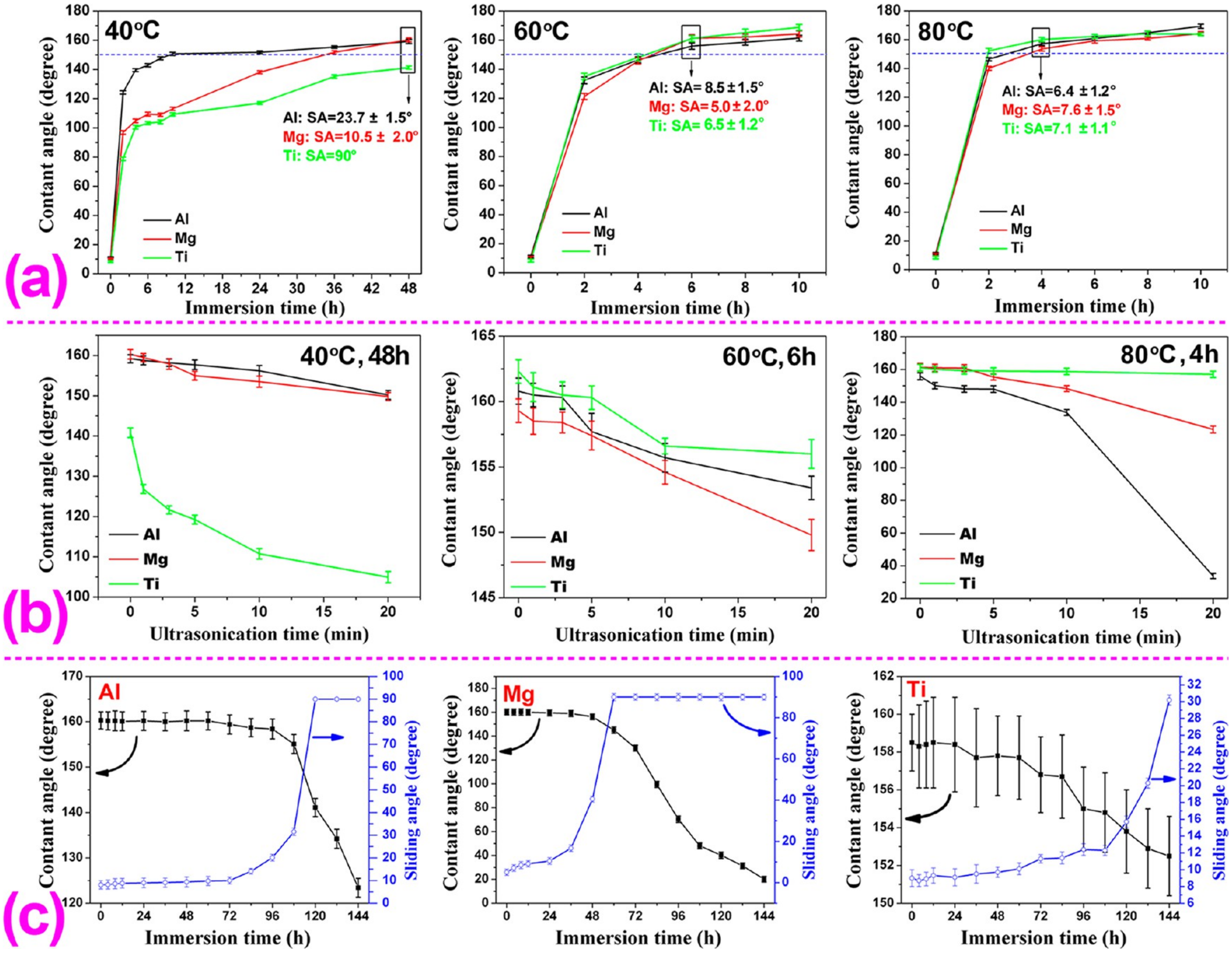

Figure 3. Evolution of SCA with (a) immersion time in the SHS fabrication process and (b) ultrasonication time in an ultrasonication process. From a and b, it can be seen that the most optimum to fabricate SHS is 60 °C/6 h (detailed discussions can be found in the text). To estimate the long-term stability of the so-fabricated SHS under such optimum condition, we (c) immersed SHS into NaCl solution for a certain period of time and then took it out and monitored the static contact angle (SCA)/sliding angle (SA) was monitored.

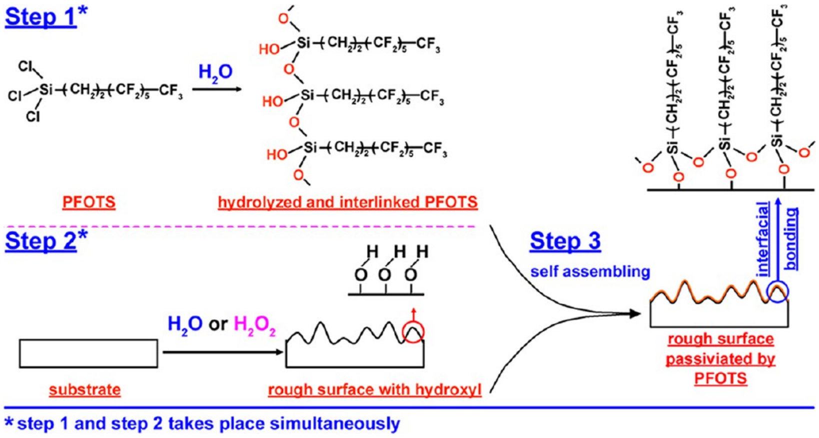

Figure 4. Possible covalent bonding mechanism of PFOTS to the substrate.

with the control samples. This may be due to the different interfacial force between the substrate and low-surface-energy molecules. Specifically, for the so-fabricated SHS in the present work, chemical interfacial bonding is expected (as to be discussed later, and Figure 4). For control samples, there generate no functional surface groups, which can react with PFOTES or its hydrolysates, on the substrate by a chemical etching process; so, weak interfacial interaction such as physical adsorption is expected. It can be well-understood that SHS with chemical interfacial bonding is more stable than SHS with interfacial physical adsorption.

The possible bonding mechanism of PFOTS molecules to the substrates under this one step process can be proposed by an analysis of the bonding energies of M 2p (M = Al, Mg and Ti, see the Supporting Information), Si 2p, and O 1s peaks. Specifically, Al 2p/Mg 2p/Ti 2p is located at 74.7/50.0/458.6 eV respectively. These values are higher than that of Al (0) (73 eV)/Mg (0) (49.4 eV)/Ti (0) (453.7 eV) and very close to that of Al (III)/Mg (II)/Ti (IV), respectively,[28] indicating that the Al/Mg/Ti elements in the surfaces are positively charged, possibly by formation of direct bonding with oxygen (as to be discussed in O 1s later). Moreover, based on the ultralow WCA close to zero for the substrates treated by $H_2O/H_2O_2-C_2H_5OH$, it is supposed that, under the attacking of H_2O (for Al and Mg alloys) or H_2O_2 (for Ti alloy), hydrophilic surface hydroxyl groups (M−OH, M = Al, Mg, and Ti) on hydroxide [$Mg(OH)_2$ or $AlO(OH)$] or oxide (TiO_2) may be generated by the following reaction equations[25]

$$Mg + 2H_2O \leftrightarrow Mg(OH)_2 + H_2$$

$$2Al + 4H_2O \leftrightarrow 2AlO(OH) + 3H_2$$

$$Ti + 2H_2O_2 \leftrightarrow TiO_2 + 2H_2O$$

Simultaneously, PFOTS molecules are expected to be hydrolyzed under the attacking of water and bonded to the so-generated surface hydroxyl groups (M−OH, M = Al, Mg, and Ti). Such a interfacial bonding process is schematically shown in Figure 4 and was thoroughly discussed in the literature earlier.[29] The formed Si−O−Si and Si−O-M can be found in Si 2p (Figure 2) and the amount ratio of former to latter is 2:1, 2.3:1, and 2.3:1 for Al, Mg, and Ti, respectively, which is the same or close to the value calculated from Step 1 of Figure 2 (i.e., 2: 1). The deconvolution of O 1s and the presence of Si−O−Si and Si−O-M also support this supposition (Figure 2).[30,31]

4. CONCLUSIONS

By a simple and universal solution immersion one-step process, SHS can be fabricated on light alloys of Al, Mg, and Ti. The key factor for this one-step process is to obtain a homogeneous solution containing both chemical etcher and low-surface-energy molecules; the former is to generate a rough surface and the latter is to passivate such rough surface. Such a key factor is of the general guide significance for the fabrication of SHS on other substrates by similar solution immersion one-step process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

XPS survey spectra for different samples treated by $H_2O/H_2O_2-C_2H_5OH$-PFOTS, and F 1s/M 2p (M = Al, Mg, or Ti) high-resolution spectra for different samples treated by $H_2O/H_2O_2-C_2H_5OH-$PFOTS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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