

# Fabrication of Superhydrophobic Silica-Based Surfaces with High Transmittance by using Polypropylene and Tetraeyoxsilane Precursors

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**ABSTRACT:** Preparation of superhydrophobic silica-based surfaces via sol-gel process by adding polyethylene glycol (PEG) polymer into the precursor solution has been developed. Surface roughness of the films was obtained by removing the organic polymer at 500°C and then the hydrophobic groups bonded onto the films were obtained by self-assembly modification with a monolayer. Characteristic properties of the as-prepared films were analyzed by contact angle measurements, scanning electron microscopy, atomic force microscopy, UV-vis scanning spectrophotometer, and X-ray photoelectron spectrophotometer. The experimental parameters were varied by the type of silane species, the *R* ratio, the hydrolysis time of the precursor solution, the molecular weight of PEG, the pH value of mixing solution, and the dif-

ferent reagents for modification. The results showed that optimum ratio of TEOS/H<sub>2</sub>O/ethanol in the sol-gel process for precursor solution was set to 1/10/4. The better contact angles of the films can be obtained by the acid catalyst reaction, especially the pH value of mixing solution was adjusted to 0. When the as-prepared rough films were modified with (tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane (TFCS), the contact angle of the film can be promoted to 150.4°, and the transmittance of the films in the visible light region was greater than 94.5%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1530–1538, 2008

**Key words:** polyethylene glycol; superhydrophobic surface; hybrid; lotus effect

## INTRODUCTION

Hydrophilic and hydrophobic surfaces are governed by both surface roughness and chemical composition. One of the famous phenomena was lotus leaf. "Lotus Effect" has its marvelous properties that possess superhydrophobic surfaces, with a water contact angle (CA) greater than 150°, and self-cleaning phenomenon. In general, the contact angles can be enhanced in two dominated elements from lotus leaf structure: One is low surface energy materials (chemical method) and the other is roughness (geometrical method).<sup>1–5</sup> Conventionally, for the hydrophilic materials, in order to form the superhydrophobic films, modification of surface chemistry is always in conjunction with enhancement of the surface roughness.

As for low surface energy substances, fluorine is the most effective element because of its small atomic radius and its electronegativity which is the largest among all atoms, so that a covalent bond could be formed with carbon in order to generate low surface energy of the surface.<sup>5</sup> This chemical modification leads to an increase in the contact angle

of water drop, with a maximum value of approximately 120° as reported for smooth CF<sub>3</sub>-terminated surfaces.<sup>4,6–8</sup> The superhydrophobic films with fluorinated-copolymer have been prepared in our laboratory.<sup>9</sup> Hare et al.<sup>10</sup> reported that the surface free energy of the substituted group in the polymer backbone increased in the order of  $-\text{CF}_3 < -\text{CF}_2\text{H} < -\text{CF}_2- < -\text{CH}_3 < -\text{CH}_2-$ . Therefore, with fluoro and methyl groups terminated surfaces, the hydrophobic property of the surfaces can be enhanced greatly.

Superhydrophobic silica-based films had been prepared by organic/inorganic hybrid method via sol-gel process.<sup>5,11–14</sup> The hybrid films were easily prepared by this method and the rough surfaces with hydrophilic property can be generated after decomposing the polymer phase at high temperature. Polyethylene glycol (PEG) polymer was chosen here because it was easily to form hydrogen bonding with the silanol group and/or form C—O—Si covalent bonds with the silica network.<sup>15–18</sup> Finally, hydrophobic property of the surfaces can be acquired by introducing the low surface energy substances to form a strong chemical bond onto the surfaces of the films.<sup>19</sup> In previous study of our laboratory,<sup>20</sup> superhydrophobic thin films have been prepared by PEG-silica hybrid solution to increase the surface roughness, but the transmittance of the films

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was very low. It was because that the thin films prepared with multilayers by the above solution which was affected the transmittance of the films greatly. However, the high contact angles of films with one-layer coating have been prepared by PPG-silica hybrid solution in another study.<sup>21</sup> To increase the transmittance of the films with one-layer coating, the preparation condition of PEG-silica hybrid solution should be reconsidered carefully. In this study, the type of silane species, the *R* ratio, the hydrolysis time of the precursor solution, the molecular weight of PEG, the pH value of mixing solution, and the different reagents for modification were discussed.

## EXPERIMENTAL

### Materials

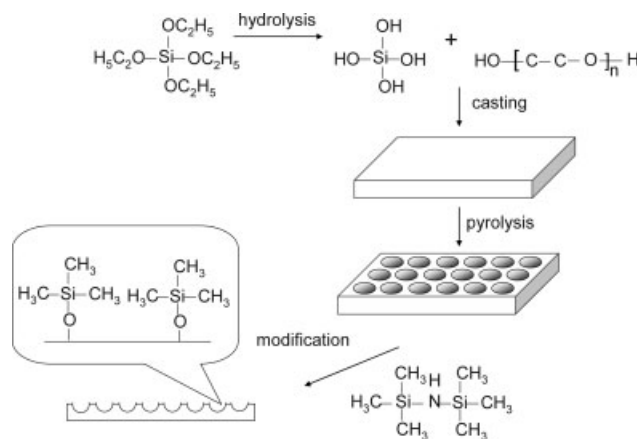
Tetraethoxysilane (TEOS, reagent grade), methyltriethoxysilane (MTEOS, reagent grade), and dimethyldiethoxysilane (DMDEOS, reagent grade) were all purchased from Shin-Etsu Chemical, Japan. Polyethylene glycol (PEG, molecular weight was 200, 400, 1000, 2000, 4000, 6000, 12,000, and 20,000, reagent grade) was all obtained from First, Taiwan. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) was purchased from Lancaster. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-dimethylchlorosilane (TFCS) was purchased from GELEST Inc. Other reagents were as follows: hydrochloric acid (HCl) (Merck, reagent grade), ethanol (EtOH) (ECHO, reagent grade).

### Sample preparation

There were two types of solutions prepared in advance. One was precursor solution prepared from mixtures with the molar composition, 1TEOS:4H<sub>2</sub>O (pH = 2):4EtOH and then reacted at 60°C. Another was PEG solution with the different molecular weight of 200, 400, 1000, 2000, 4000, 6000, 12,000, and 20,000, was prepared by mixing with 50% PEG in ethanol solution. Further, the mixing solution was prepared by mixing above two solutions (the weight ratio of PEG solution to precursor solution was set to 3) which heated at 60°C for 2 min and then cooled at 18°C for 1 min. The other precursor solutions with MTEOS and DMDEOS were also prepared by using the same method as above condition. Finally, the different pH value of mixing solution was to adjust to 0, 1, 2, 6, and 8.

### Preparation of thin films

The substrates, slide glasses were vacuum-locked during the spin-coating process. A chemical substrate cleaning procedure was ultrasonicated for 30 min with HCl (0.1N), NaOH (0.1N), deionized water,



**Scheme 1** Schematic of the procedure on the preparation of superhydrophobic films.

and iso-propylalcohol, respectively. The uniform films were prepared at a spinning rate of 4500 rpm for 15 s with spraying the mixing solution onto the clean substrates. In all cases, hybrid films were reacted at 250°C for 2 h and then raised the temperature to 500°C for 2 h. The surface chemistry of the films was modified with self-assembly monolayer by two methods: One was using HMDS solution which prepared by dissolving HMDS in toluene and the concentration of it was 10 wt %. The self-assembly time and temperature of the solution was 6 h and 110°C, respectively. The other was immersed with 10% TFCS in ethanol solution for 1 day and then dry at 60°C for 1 h. The whole procedure of preparation of superhydrophobic thin films was sketched in Scheme 1.

### Instrumentation

Surface morphologies of the films were observed under scanning electron microscopy (SEM, Hitachi S-4200) and the variation of roughness was analyzed by atomic force microscopy (AFM, Seiko SPA400) with tapping mode. Water contact angles of prepared films were measured using manual contact angle goniometer (Kyowa interface sciences CA-D) as follows: water droplet was gently placed onto the films and the average value measured over five different locations for each sample was taken. By applying the  $\theta/2$  method and regulating the droplet size to about 20 scale and observed through the eyepiece; the difference between average contact angle and five different located contact angles was  $\pm 2^\circ$  in this study. The optical transmittance was determined by UV-vis scanning spectrophotometer (JASCO V-530). The composition of the treated surfaces was studied by X-ray photoelectron spectroscopy (XPS, VG Sigma Probe).

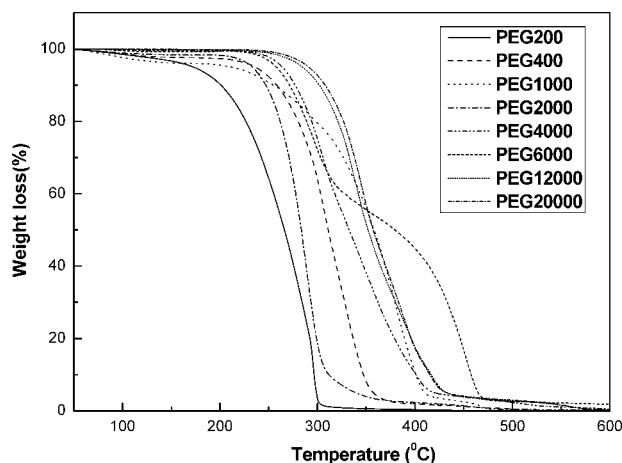


Figure 1 TGA result of PEG polymers.

## RESULTS AND DISCUSSION

In this study, the silica-PEG hybrid mixing solution was prepared by mixing precursor solution (inorganic part) and PEG solution (organic part). The above mixing solution was further reacted to form silica-PEG network with PEG—C—O—Si covalent and/or PEG—OH••OH—Si— hydrogen bonds form.<sup>22–25</sup> Chen studied PEG/SiO<sub>2</sub> hybrid materials via sol-gel process by DSC showed that with increasing PEG weight fraction of hybrid materials, there were many PEG rich domains in the hybrid materials.<sup>24</sup> Therefore, after casting the solution onto the substrates, surface roughness was enhanced by decomposition of PEG at high temperature. The TGA results of PEG polymers with different molecular weight were shown in Figure 1. The curve of PEG was shifted to higher temperature region with increasing the molecular weight of PEG, implying that the decomposition rate of higher molecular weight of PEG was slower than that of the lower molecular weight. In addition, the weight loss of PEG polymer had been almost finished before 500°C. Therefore, the temperature of removing PEG polymer from the films was set to 500°C that made sure only inorganic materials was existed on the surfaces and the structures of the network on the films was not destroyed.

To investigate the preparation conditions on the films, the silane species, the *R* ratio, the hydrolysis time of the precursor solution, the molecular weight of PEG, the pH value of mixing solution, and the different reagents for modification were discussed.

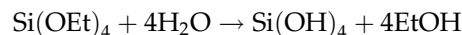
### Silane species

There were three kinds of silane for preparation in this research. The effect of the contact angles of the films prepared by different parameters in the sol-gel

process was shown in Table I. When compared with the sample numbers 1, 2, and 3, it was indicated that the contact angles of the films prepared by TEOS was higher than that by MTEOS and DMDEOS. It was considered that there were four functional groups in the TEOS structures to become hydroxyl groups after hydrolysis reaction and then to form network in the hybrid materials after polycondensation reaction, so the dense and rough structures can be acquired after the decomposition of PEG polymer at high temperature. On the other hand, when the films were prepared by MTEOS or DMDEOS silanes, there were three hydroxyl and one methyl groups in the MTEOS structure and two hydroxyl and two methyl groups in the DMDEOS structure after completely hydrolysis reaction, respectively. Therefore, the crosslinking density of the hybrid materials prepared by MTEOS and DMDEOS was less than that by TEOS. The same result was also reported by Dahmouche et al.<sup>26</sup> In addition, the methyl groups of MTEOS and DMDEOS on the films were decomposed to become hydroxyl group and PEG polymer was also almost completely decomposed when the temperature was increased to 400°C, then the rough surfaces of the films were easily destroyed to become the smooth surfaces by further condensation of these hydroxyl groups. As mentioned earlier, the TEOS silane was chosen as inorganic part to prepare the film.

### The *R* value

The *R* value in the sol-gel process means the molar ratio of water to alkoxide and this ratio also influences the reaction rate greatly. The stoichiometric *R* value for complete hydrolysis is 4 as show below:<sup>27</sup>



On comparing with the sample numbers 1, 4, and 6 as shown in Table I, the different *R* value (4, 6, and 10) in the sol-gel process exhibited the different

TABLE I  
The Preparation Conditions and Characteristics of the Films

Run no.	Silane <sup>a</sup>	<i>R</i> <sup>b</sup>	Reaction time (h)	Contact angle (°)
1	TEOS	4	4	123.9
2	MTEOS	4	4	122
3	DMDEOS	4	4	106.9
4	TEOS	6	4	124.1
5	TEOS	10	2	123.8
6	TEOS	10	4	127.7
7	TEOS	10	6	120.3
8	TEOS	10	8	119.8

<sup>a</sup> Silane:H<sub>2</sub>O(pH = 2):EtOH = 1:4:4; the hydrolysis reaction at 60°C for 4 h.

<sup>b</sup> *R* was the mole ratio of H<sub>2</sub>O/silane.

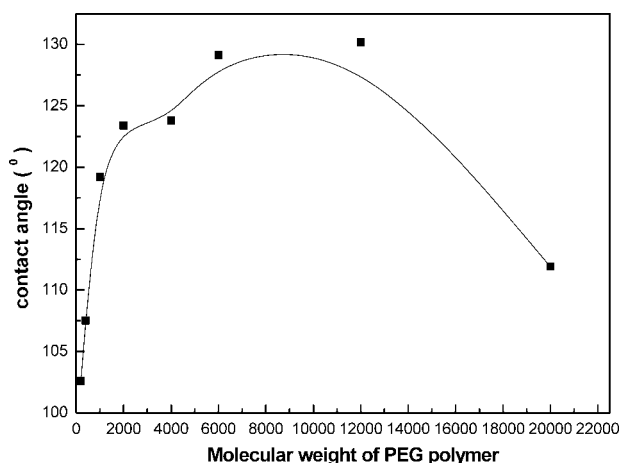
results of contact angles. It was indicated that the contact angles of films prepared by the ratio of 10 was higher than that of 4 and 6, meanwhile, the contact angles of films prepared by the ratio of 4 and 6 seem to be the same. It was considered that the hydrolysis rate was increased with increasing  $R$  value because of the raised reactant concentration. Although less water can be used since the condensation reaction leads to production of water,<sup>27</sup> the partial hydrolysis of TEOS precursor could lead to uncompleted reaction. So, the lower  $R$  value was resulted in more smooth surfaces because of the less crosslink of polycondensation reaction. On a contrary, increasing the  $R$  value which generally promotes hydrolysis reaction, large amount of water is effectively diluted and promoted gel time increasingly.<sup>27</sup> In addition, the volume of hybrid materials was also increased to easily prepare the rough surfaces because the large amount of water was evaporated. Therefore, the  $R$  value of 10 was favored for next-up experimental stages.

#### The hydrolysis time of the silane precursors

In a typical sol-gel process, the precursor is accompanied with a series of hydrolysis and polycondensation reactions to form a colloidal suspension. Therefore, with the time goes pass, gelation occurs when links form between silica sol particles.<sup>27</sup> It was considered that with increasing the hydrolysis time of precursors, the viscosity of solutions became higher so that the coating films could be influenced. To investigate this effect, the contact angles of the films prepared by different hydrolysis time of the precursor solutions as sample numbers 5, 6, 7, and 8 in Table I. With increasing the hydrolysis time of precursor solutions from 2 to 8 h, the hydrolysis time of 4 h was exhibited an excellent result, which has contact angle of the film of 127.7°, was higher than others. It was considered that the higher viscosity of precursors resulted from long-time of reaction and the surface roughness could be promoted. But the more homogeneous coatings were due to lower viscosity of mixing solution and the smoother surfaces could be acquired. Therefore, four hour was a suitable hydrolysis time to prepare the films with higher contact angles.

#### Molecular weight of PEG polymers

The roughness of the films was obtained by the decomposition of PEG at high temperature, so molecular weight of PEG polymer in the sol-gel process were very important to be discussed. Effect of contact angles of the films on these factors were shown in Figure 2. The contact angles of the films were increased with increasing the molecular weight of PEG polymer from 200 to 12,000, but the contact

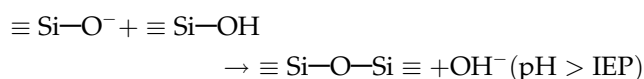
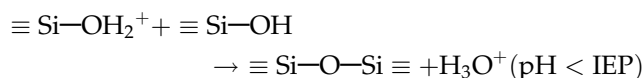


**Figure 2** Contact angles of the films prepared by the different molecular weight of PEG polymer, 200, 400, 1000, 2000, 4000, 6000, 12,000 and 20,000.

angles of the films prepared by the molecular weight of 20,000 was dropped rapidly. It was considered that there were many PEG rich domains in the hybrid materials with increasing the molecular weight of PEG. After decomposition of PEG at high temperature, surface roughness can be enhanced easily because of phase separation phenomenon. But for too higher molecular weight of PEG polymer (e.g. MW = 20,000), it was easily led to the viscosity of mixing solutions become too high, so the unhomogeneous coatings were easy to obtain. Therefore, when the decomposition of as-prepared films was occurred, the surfaces of the films were easily destroyed. When compared with the molecular weight of 6000 and 12,000, the contact angles of the films were almost near 130°. It was an excellent data for further study to prepare superhydrophobic surfaces.

#### Adjustment of contact angles with different pH value

In general, condensation reaction of sol-gel process was quite slow when the pH value was about 2 (the point of zero charge (PZC) where the surface charge is zero; isoelectric point (IEP)), implying that the gel time was very long.<sup>28</sup> The rate coefficient of condensation is lowest when  $\text{pH} = \text{IEP}$ .<sup>28</sup> It was because that the reaction mechanism changes from the attack of neutral silanol on the protonated silanol ( $\text{pH} < \text{IEP}$ ) to the attack of deprotonated silanol on the neutral silanol ( $\text{pH} > \text{IEP}$ ) as shown below:<sup>29</sup>



**TABLE II**  
**Contact Angles of the Films Were Prepared by the PEG6000 and PEG12000 Polymer with Adjusting Different pH Value of Mixing Solution**

Run no. <sup>a</sup>	R <sup>b</sup>	Reaction time <sup>c</sup> (h)	Molecular weight of PEG polymer	pH <sup>d</sup>	Contact angle (°)
9	10	4	6000	0	139.2
10				1	130.7
11				2	124.5
12				6	124.9
13				8	129.1
14			12,000	0	147.4
15				1	128.3
16				2	126.5
17				6	128.2
18				8	130.2

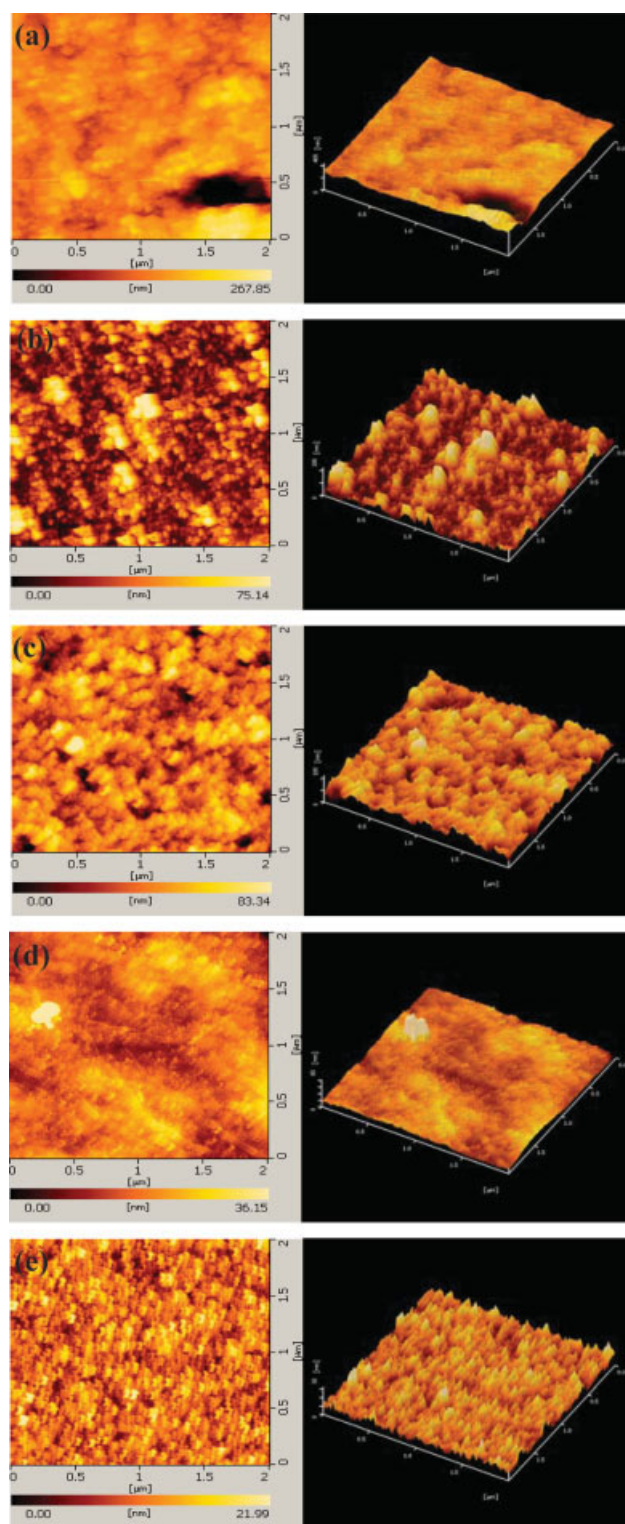
<sup>a</sup> TEOS:H<sub>2</sub>O(pH = 2):EtOH=1:10:4.

<sup>b</sup> R was the mole ratio of H<sub>2</sub>O/TEOS.

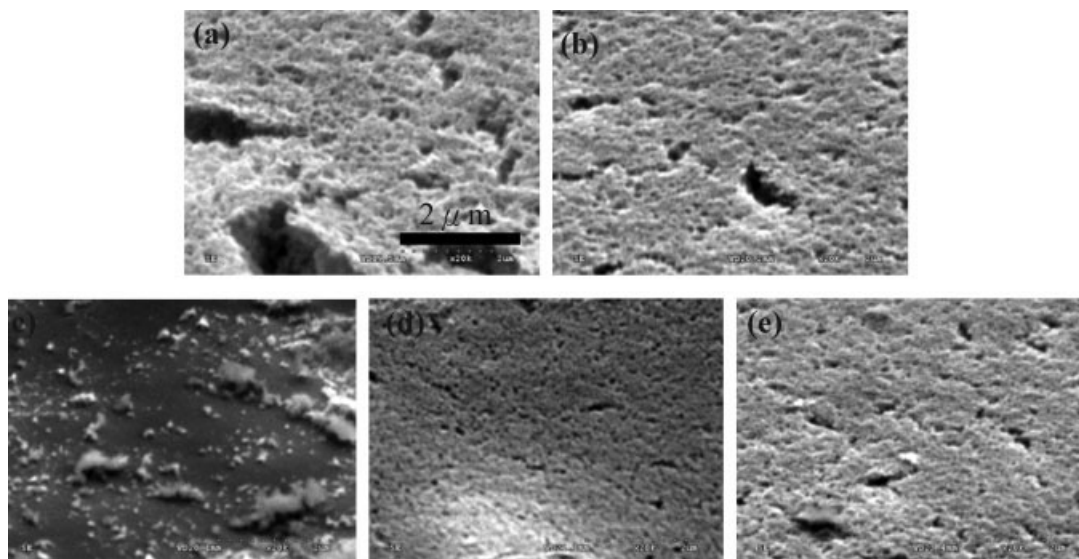
<sup>c</sup> The hydrolysis reaction at 60°C for 4 h.

<sup>d</sup> Adjusting the different pH value of mixing solution.

To increase the phase separation of silica, increasing and decreasing the pH value (far away from 2) were the method to accelerate the condensation reaction and shorten the gel time. Effect of the contact angles of the films prepared with different pH value of mixing solution on the different molecular weight of PEG polymers was shown in Table II. For both molecular weight of 6000 and 12,000, it was all indicated that the contact angles of the films were decreased and then increased with increasing the pH value of mixing solution from 0 to 8. The contact angles of the films was lowest when the pH value of the mixing solution was 2, but the others (pH = 0, 1, 6, 8) were greater than it. It was considered that with increasing and decreasing the pH value of mixing solution, the phase separation was occurred easily so that the surface roughness was promoted. Besides, the contact angles of the films prepared by acid (pH = 0, 1) conditions was almost greater than that by base (pH = 6, 8) conditions. In the sol-gel process, formation of linear structures was easily occurred by the acid catalyst reaction, but monolithic gels were appeared<sup>30</sup> because of base catalyst condition. Therefore, the more homogenous and dense thin films can be obtained by decreasing the pH value to acid condition than that by increasing the pH value to base condition. It was because that the linear structures of SiO<sub>2</sub> can be deposited onto the surfaces easily and homogeneously. When the pH value of mixing solution was 0, the excellent contact angles of the films can be obtained. It was indicated that the molecular weight of 12,000 was 147.4° and that of 6000 was 139.2° as shown in Table II. Therefore, the better contact angles of the films can be



**Figure 3** 3D AFM images on the surfaces of the films prepared by the PEG12000 polymer and TEOS with adjusting different pH value of mixing solution. (a) pH = 0, Ra = 82.79 nm, (b) pH = 1, Ra = 39.02 nm, (c) pH = 2, Ra = 23.86 nm, (d) pH = 6, Ra = 36.46 nm, (e) pH = 8, Ra = 34.17 nm. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** SEM images on the surfaces of the films prepared by the PEG12000 polymer and TEOS with adjusting different pH value of mixing solution. (a) pH = 0, (b) pH = 1, (c) pH = 2, (d) pH = 6, (e) pH = 8.

obtained easily when the pH value of mixing solution was adjusted to 0. It was concluded that the better contact angles of the films can be prepared by acid condition, especially the pH value was 0.

To realize the relationship between contact angle and pH value of mixing solution, surface morphology and microstructures were measured by AFM and SEM with PPG molecular weight of 12,000. From the AFM image as shown in Figure 3, the surface roughness was decreased first and then increased with increasing the pH value of mixing solution from 0 to 8. It was indicated that the roughness degree was biggest at the Ra was 82.79 nm when the pH value of mixing solution was 0 as shown in Figure 3(a), implying that the more rough surfaces were appeared so that the data of contact angles was highest. And then the minimum was appeared when the pH value of mixing solution was 2 as shown in Figure 3(c), implying that the contact angles of the films was dropped greatly at this point. With increasing the pH value of mixing solution from 2 to 8, the roughness was increased gradually as shown in Figure 3(d,e). It was led to increase the contact angles of films. From the SEM images as shown in Figure 4, the microstructures of the surfaces can be acquired from the microscopic view when the pH value of mixing solution was from 0 to 8. It was indicated that the quite rough and dense surfaces was obtained when the pH value of mixing solution was 0 as shown in Figure 4(a), therefore, the contact angle of the film was the biggest one, 147.4°. In addition, the porous and rough composition was combined with the more linear structures of SiO<sub>2</sub> at this time. With increasing the pH value of mixing solution to 1 as shown in Figure 4(b), the dense

structures were still appeared so that the contact angles of the films was still high. With increasing the pH value of mixing solution to 2 as shown in Figure 4(c), the quite plate and smooth surfaces can be obtained resulted in decreasing the contact angles of the films. When the pH value of mixing solution was increased from 2 to 8 as shown in Figure 4(d,e), the dense and rough structures was appeared again so the surface roughness was also led to increase the contact angles of the films. Therefore, it can be concluded that the contact angles of the films were promoted greatly when the pH value of mixing solution was 0 from the data of SEM and AFM.

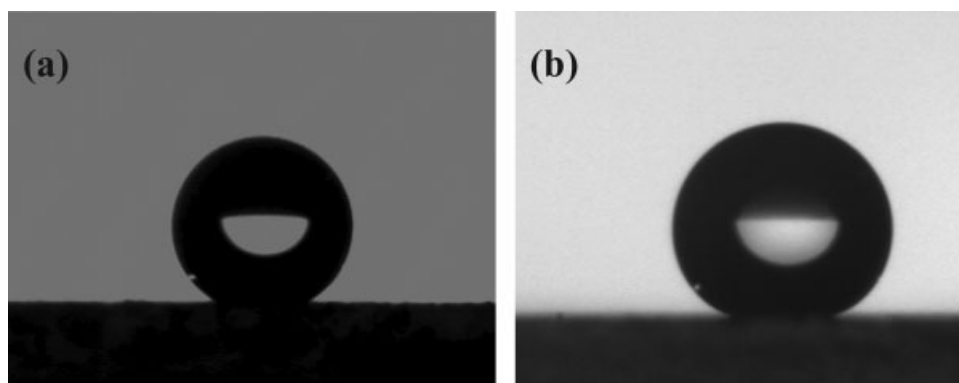
In the sol-gel process, acid catalysis causes faster hydrolysis of TEOS and the morphology of the product is weakly branched. On the contrary, faster condensation occurs in a basic catalytic system and the morphology of the product is of particle type. Hence the morphology of the silica will influence the properties of the hybrid materials. Furthermore, the roughness of films also increased accompanied with the degree of phase separation increased. Therefore, linear structures of silica were formed under the

**TABLE III**  
Contact Angle of the Film Prepared by the Surface Modification of Different Self-Assembly Substance

Run no.	Hydrophobic substance	Contact angle (°)	
		PEG6000	PEG12000
19	HMDS <sup>a</sup>	139.2	147.4
20	TFCS <sup>b</sup>	144.2	150.4

<sup>a</sup> Reflux with 10 wt % HMDS solution at 110°C for 8 h.

<sup>b</sup> Immersion with 10 wt % TFCS solution at 60°C for 1 day.



**Figure 5** Image of water drop on the surfaces of the films prepared by the TEOS and PEG12000 polymer with two different modified method, (a) reflux with HMDS solution and (b) immersion with TFCS solution.

condition of  $\text{pH} < 2$  and produced the homogenous organic/inorganic hybrid material. After pyrolysis process, the continuous porous surface was formed then the higher roughness and contact angle of film was also obtained. In the contrary, dense particle structure of silica and a little nonhomogeneous hybrid material were formed when  $\text{pH} > 2$  so that the rough surface become a little noncontinuous after pyrolysis process. Finally, the roughness and contact angle of films under base condition were smaller than acid.

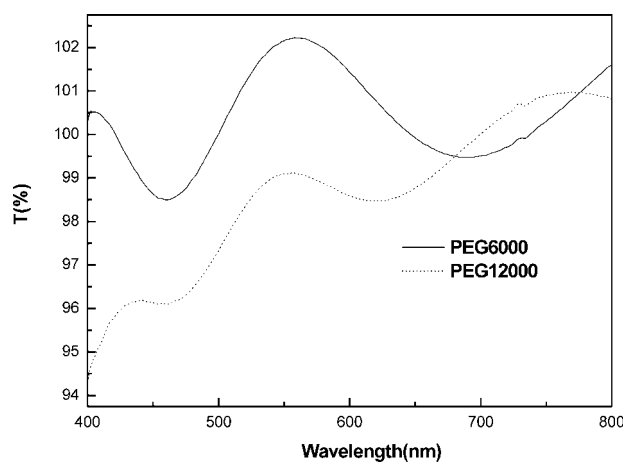
What the passage made clear at once was indicated that the contact angles of the films were lowest when the pH value of mixing solution was 2. However, the contact angles of the films were increased when the pH value was far away 2, especially the pH value was 0.

#### The different reagents for modification

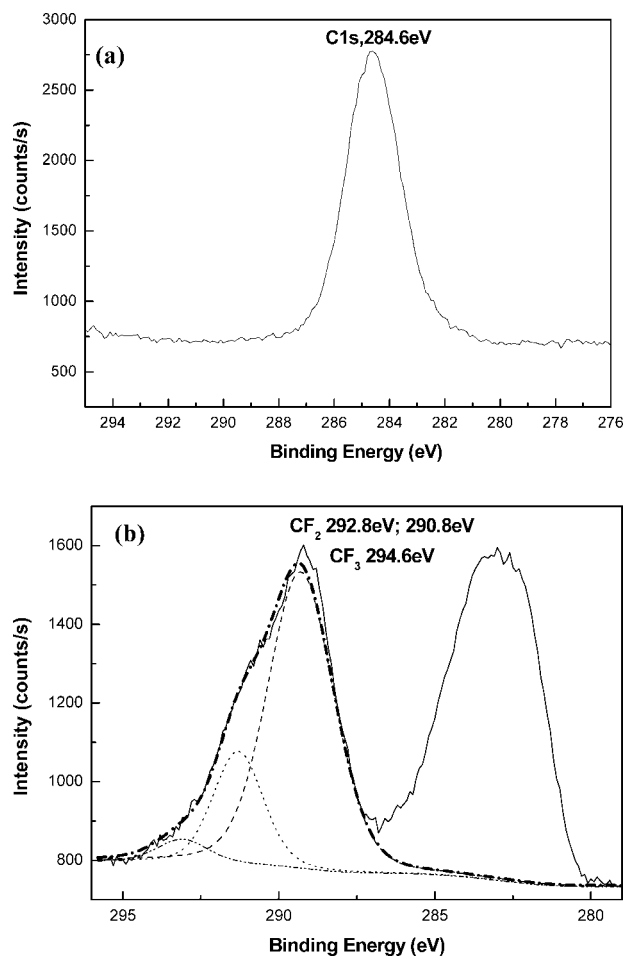
From the above data, the better results can be obtained by using proper ratio of precursor solution (TEOS:H<sub>2</sub>O:EtOH = 1:10:4), the molecular weight of PEG polymer (6000 and 12,000), and the pH value of mixing solution ( $\text{pH} = 0$ ). It was indicated that the contact angle of  $147.4^\circ$  can be prepared by modification of HMDS. Herein, hydrophobic substituent groups were replaced in order to increase the contact angles of the films. TFCS with fluoro-terminated groups was the lower surface energy materials than methyl-terminated groups of HMDS. Therefore, the monolayer of hydrophobic substances was modified by immersion with TFCS for 1 day.<sup>31</sup> The results were shown in Table III. When the films were prepared by TEOS and PEG12000, the contact angles of the films prepared by the modification of HMDS was  $147.4^\circ$  but that of TFCS was promote to  $150.4^\circ$ . It was due to the fluoro-groups increased the hydrophobic property of the surfaces. The pictures of water drop on the films with different method of modification were shown in Figure 5. The superhy-

drophobic thin films can be prepared when the rough surfaces were modified by TFCS. On the other hand, the transmittance of the films in the visible light region with the wave length from 400 to 800 nm was shown in Figure 6. It was indicated that the transmittance of the films prepared by TEOS and PEG6000 was almost 100% but that by TEOS and PEG12000 was greater than 94.5%. It was considered that only one-layer coatings could affect and increase the transmittance of the films. Therefore, the films contained superhydrophobic and transparent properties simultaneously can be prepared by using TEOS and PEG12000, meanwhile, surface modification was perfect for using fluoro-terminated groups of TFCS.

To confirm the existence of substituent groups on the outermost layer of the as-prepared thin films, XPS spectrum was obtained to study as shown in Figure 7. The result showed that C 1s spectrum of the rough surfaces with treatment of HMDS as shown in Figure 7(a). The single peak centered at 284.6 eV supported that modification had successfully



**Figure 6** Transmittance of the films prepared by the two different molecular weight of PEG polymer with modification of TFCS, which was detected with visible light wavelength range from 400 to 800 nm.



**Figure 7** XPS spectrum of as-prepared thin film. (a) C 1s of the film was modified by HMDS and (b) CF<sub>x</sub> of the film was modified by TFCS.

introduced hydrophobic groups onto the rough surfaces. But for realizing the existence of fluorine containing groups of TFCS onto the surfaces, a least-square curve fitting program was used for splitting into several subpeaks of functional groups. A typical splitting of C 1s spectrum was shown in Figure 7(b). The peaks in the spectrum can be ascribed to CF<sub>2</sub> groups at 292.8 eV and 290.8 eV, in addition, CF<sub>3</sub> groups at 294.6 eV.<sup>32</sup> Therefore, the surface modification indeed contained the fluoro-terminated groups.

## CONCLUSIONS

Hydrophilic silica-based surfaces have been prepared by a hybridization of TEOS and PEG polymer with suitable conditions and then the surface roughness was promoted by removing PEG polymer from the films. For precursor solution (the sol-gel process): the type of silane species was set to TEOS, the *R* ratio was set to 10, and the hydrolysis time was set to 4. But for PEG polymer, the better contact

angles of the films can be prepared by the molecular weight of 12,000. In addition, the contact angles of the films were varied by the pH value of mixing solution from 0 to 8, but the better result was appeared when the pH value was adjusted to 0. For the above optimum condition, the contact angles of as-prepared rough films were modified by two ways: one was refluxed with HMDS for 6 h and the other was immersed with TFCS for 1 day. The results showed that the contact angles of the films modified by HMDS (methyl groups) were 147.4°, but that modified by TFCS (fluoro groups) was promoted to 150.4°. When the films contained the superhydrophobic property, the transmittance of the films in the visible light region was greater than 94.5% at the same time.

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