Preparation of Superhydrophobic Silica-Based Films by Using Polyethylene glycol and Tetraethoxysilane

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ABSTRACT: Preparation of superhydrophobic silica-based films via sol-gel process by adding polyethylene glycol (PEG4000) in the silica sol precursor solution has been developed. The casting films were prepared by casting the above solution on the glass and adding poor solvent on it or not. Surface roughness of the films was obtained by removing polymer from the films at high temperature. Then, the hydrophobic group on the surfaces was obtained by reaction with hexamethyldisilazane (HMDS). Characteristic properties of the as-prepared surface of the films were analyzed by contact angle measurement, scanning electron microscopy (SEM), atomic force microscope (AFM), Fourier transform infrared (FT-IR) spectrophotometer, and X-ray photoelectron spectrometer (XPS). The results showed that the contact angles of the films were varied with the PEG weight fraction of the films, the solvent for the PEG solution, the reaction temperature and time, and adding poor solvent (n-hexane) or not. However, the surface roughness has been controlled by adjusting the experimental parameters during the early period. The contact angle of the film that prepared by spraying the poor solvent (n-hexane) onto each coating layer for four times after casting process was greater than $150°$. It was difficult to obtain superhydrophobic surface without adding n-hexane onto any coating layer in this system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1503–1510, 2007
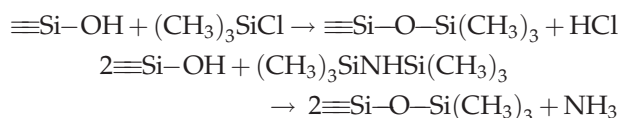
Key words: polyethylene glycol(PEG); superhydrophobic; poor solvent; lotus effect

INTRODUCTION

''Lotus Effect'' has its marvelous properties that possess superhydrophobic characteristic and self-cleaning phenomenon. Up to date, many studies have pointed out that superhydrophobic property must constitute two important elements: One is low surface energy substances and the other is surface roughness. Therefore, surface energy and surface roughness are the dominated factors that influence the performance of surface property.[1–5] Conventionally, two strategies are adopted, one is roughening the surface of hydrophobic materials,[6–7] and the other is forming a rough surface first and then modifying the rough surface with a special low surface energy material.[8,9] However, for the hydrophilic materials, to form the superhydrophobic films, modification of surface chemistry is always in conjunction with enhancement of surface roughness.

Hare et al.[10] reported that the surface free energy of the substituted group in the polymer backbone increased in the order of $-CF_3 < -CF_2H < -CF_2-$ $< -CH_3 < -CH_2-$. The van der waals force of the bare-fluorinated chemical compound against the substrates is very weak and hence it is necessary to synthesize with other materials. Most of the bare-fluorinated substances are the expensive materials and often vulnerable to environment attacks while causing ozone shield to crack more seriously. However, the other hydrophobic group was chosen to reduce the cost and increase the practicality. The chemical modification leads to an increase in the contact angle of water drop, with the modification of CH_3-terminated surfaces.[11] To enhance hydrophobic properties of the as-prepared surface that is usually subjected to a supplementary end-capping by means of trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) for eliminating the hydrophilic groups. The TMCS and HMDS reacted with Si—OH that was showed as following:

$$\equiv Si-OH + (CH_3)_3SiCl \rightarrow \equiv Si-O-Si(CH_3)_3 + HCl$$
$$2\equiv Si-OH + (CH_3)_3SiNHSi(CH_3)_3$$
$$\rightarrow 2\equiv Si-O-Si(CH_3)_3 + NH_3$$

It is generally known that increasing the roughness of a hydrophobic surface would increase its hydrophobicity dramatically.[12] Over the past few years, most papers are devoted to discover approaches on enhancement of surface roughness. Synthetic superhydrophobic surfaces have been fabricated through various approaches, including sol-gel method,[5,13] organic/inorganic hybrid method,[14,15] CVD method,[16] electrochemical method,[17] embossing method,[18] plasma

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method,[19] phase separation method,[3,12,20,21] and template method.[22–24]

In this research, superhydrophobic silica-based films were prepared by adding polyethylene glycol (PEG4000) into the silica sol precursor solution via sol-gel process. First, PEG4000 polymer was chosen as a preformed polymer to form a hybrid with silica sol precursor because it is crystallizable and has terminal hydroxyl groups to form hydrogen bonding with the silanol group and/or form C—O—Si covalent bonds with the silica network.[25–28] When the suitable concentration and molecular weight of PEG was chosen, the gelation of PEG-silica network was easily formed. Second, after casting it to form films, the PEG phase can be removed at high temperature and rough surfaces with hydrophilic property can be generated. Finally, HMDS was introduced to react with as-prepared films during the coating process to form a strong bond of CH_3 group onto the surface of the film.[11] The methyls, meanwhile, will bond with the surface of substrate, that the superhydrophobic property of the films can be obtained.

In this study, the PEG weight fraction of the films, reaction temperature, reaction time, and solvent for PEG solution were discussed. In addition, to increase the rough surface, the multi-layer of films by casting organic–inorganic solution onto the glass substrates several times and adding n-hexane (poor solvent) onto the coating layer to cause early phase separation on the films were also discussed.
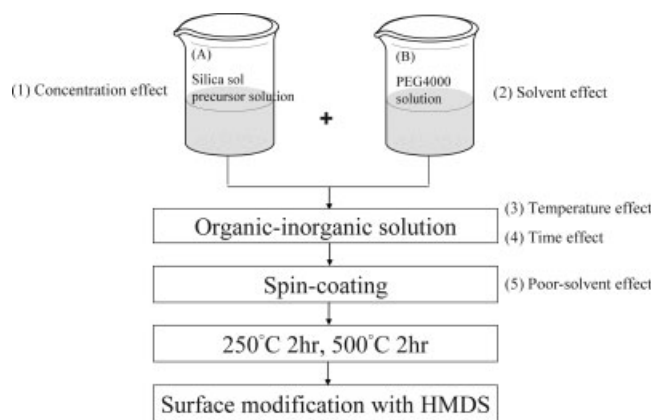
EXPERIMENTAL SECTION

Materials

Tetraethoxysilane (TEOS, reagent grade) was purchased from Shin-Etsu Chemical, Japan. Polyethylene glycol of molecular weight 4000 (PEG4000, reagent grade) was obtained from First, Taiwan. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) was purchased from Lancaster. Other reagents are as follows: Hydrochloric acid (HCl) (Merck, reagent grade), methanol (MeOH) (ECHO, reagent grade), ethanol (EtOH) (ECHO, reagent grade), toluene (TEDIA, reagent grade) and n-hexane (NASA, certified grade).

Sample preparation

There were two types of solutions prepared in advance. One was silica sol precursor solution (A) prepared from mixtures with the molar composition: 1 TEOS: 4 H_2O (pH = 2): 4 EtOH and reaction at 60°C for 4 h. Another was PEG4000 polymer solution (B), prepared from mixtures 10–100% of PEG in ethanol. On the other hand, the organic–inorganic solution was prepared by mixing above two solution, A and B (A/B = 1/1–1/5) which heated at 60°C for 2 min

**Scheme 1** The experimental process and parameters of preparation of superhydrophobic films.

and then cooled at 18°C for 1 min. 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, and isopropylalcohol, respectively. A uniform coating was prepared at a spinning rate of 4500 rpm for 15 s with spraying the organic–inorganic solution onto the clean substrates. In all cases, casting films were reacted at 250°C for 2 h and then raised the temperature to 500°C for 2 h. The surface chemistry of all the films was modified with self-assembly monolayer by using HMDS solution 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 experimental process and parameters of preparation condition were summarized in Scheme 1 and the whole procedure of preparation of superhydrophobic thin film was sketched in Scheme 2.

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. AFM analysis of the thin films was obtained by Both Root Mean Square (RMS) roughness. The RMS roughness is calculated according to the following equation:

$$RMS = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{av})^2}{N}}$$

where Z_i is the height of individual point i, Z_{av} is the average height of the entire region, and N is the number of points measured within a give area.
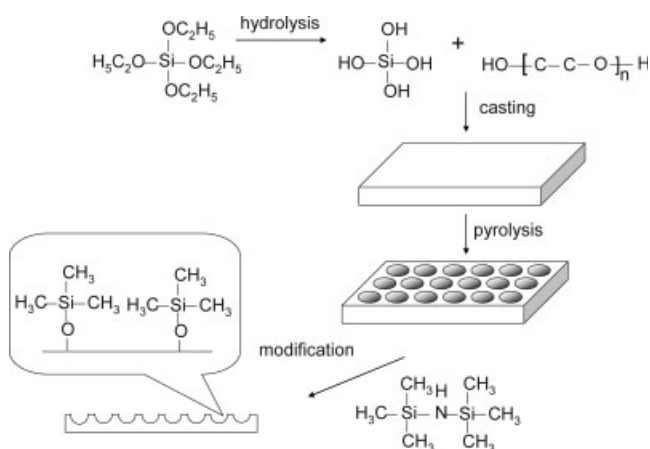
Scheme 2 Schematic of the procedure on the preparation of superhydrophobic films.

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 location for each sample were taken. By applying the $\theta/2$ method and regulating the droplet size to about 20 scale and observed through the eyepiece. The composition of the treated surface was studied by X-ray photoelectron spectroscopy (XPS, VG Sigma Probe) and Fourier transform infrared spectrometer (FT-IR, JASCO FT/IR-410).

RESULTS AND DISCUSSION

In this study, silica sol precursor solution (A) and PEG4000 solution (B) were the two base solutions to form an organic–inorganic solution. The organic–inorganic solution was further reacted and became gel during some reaction time, while the hydroxyl groups of PEG was reacted to form hydroxyl binding with silanol group and form C—O—Si covalent bonds with silica network.[25–28] Chen studied PEG/SiO$_2$ 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.[27] Therefore, after casting the solution onto the substrates, surface roughness was obtained by decomposition of PEG at high temperature. To investigate the preparation conditions on the films, the PEG weight fraction of the films, the solvent for the PEG solution, the reaction temperature and time for the casting solution, and the effect of the poor solvent, n-hexane, on the films were discussed.

The TGA and DTG diagram of PEG polymer were shown in Figure 1. The thermal degradation profiles of PEG from TGA revealed that most of the

degradation events occurred between 250 and 400°C. Therefore, DTG diagram of PEG showed the peak, at 334°C, which indicated the temperature of the maximum thermal degradation rate of the PEG. It was considered that the temperature of removing PEG was set to 500°C that made sure only inorganic material in the presence of the films and the structure of the networks in the films were not destroyed.

PEG weight fraction of the films

First, the films were prepared by organic–inorganic solution with mixing the different weight part of A and B. The effect of the contact angles of the films on the equal weight part of A and B was shown in Figure 2(A). With increasing the PEG weight fraction in the PEG solution to 40% (PEG/SiO$_2$ = 3.09), the contact angles of the films was increased. It was considered that the roughness and porosity of the films was improved by increasing the composition of PEG in the films. But the contact angles of the films kept almost a steady value when the PEG weight percentage in the PEG solution was greater than 40% (PEG/SiO$_2$ = 3.09). Therefore, to investigate the effect of PEG in the films, the films were prepared by mixing the one weight part of A and three weight part of B and the contact angles of the films were shown in Figure 2(B). The same phenomenon was also observed in the diagram, but the value of the contact angles of the films was slightly increased. It was considered that viscosity of organic–inorganic solution prepared by three weight part of B was higher than that prepared by one weight part of B and the gel time of the former casting solution was shorter than that of the latter solution. In addition, these results showed that the high value of con-
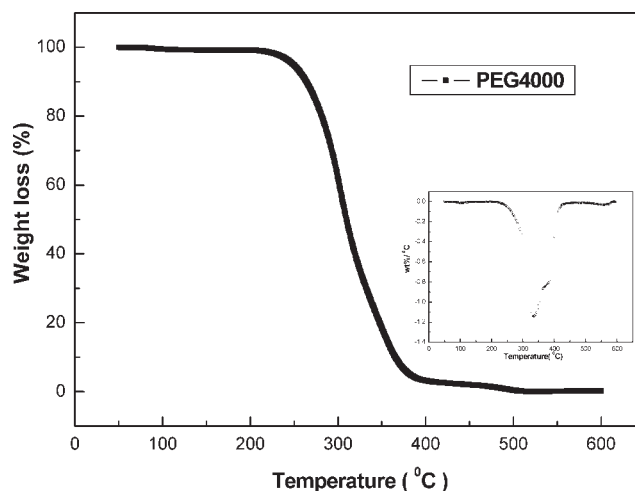

Figure 1 TGA and DTG (inside the diagram) results of PEG 4000.
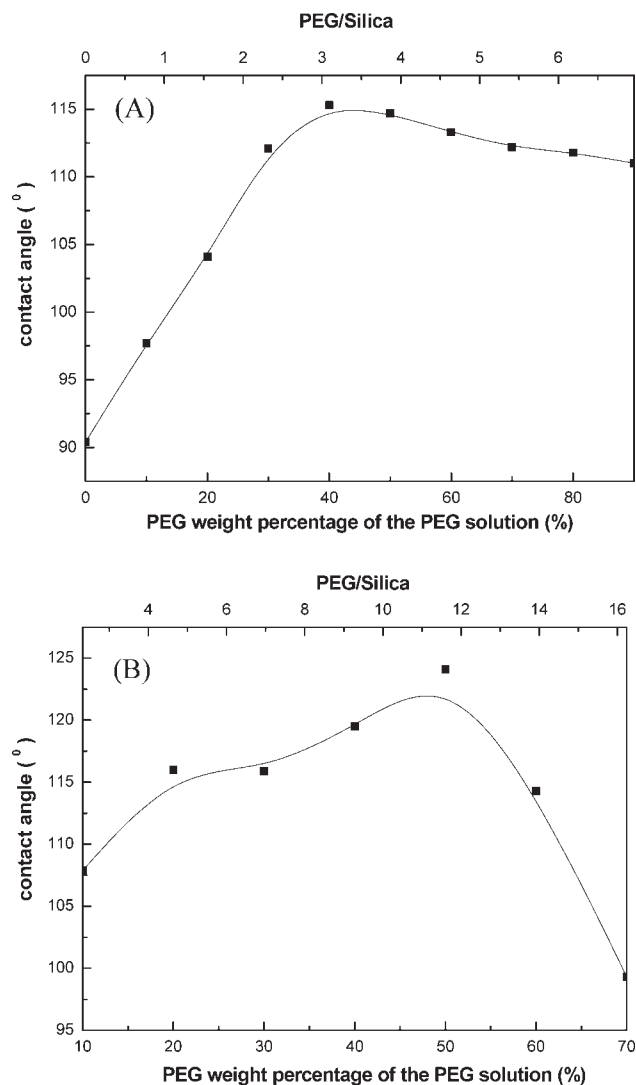
Figure 2 Effect of contact angles of the films on the PEG weight fraction in the PEG solution and the ratio of PEG to silica in the film. The organic–inorganic solution was prepared by mixing with one weight part of silica sol precursor solution and (A) one weight part of PEG solution; (B) three weight part of PEG solution.

tact angles of the films was obtained when the PEG weight percent in the PEG solution was 50% (PEG/SiO_2 = 11.60). When the PEG weight percentage was greater than 50%, the contact angles of as-prepared films were decreased rapidly. From the above data, it can be concluded that high value of contact angles of the films was able to be prepared by mixing suitable part of B in the casting solution.

The TGA curves of casting films prepared by different PEG weight percentage in B was shown in Figure 3. With increasing the PEG weight fraction from 10 to 60% (PEG/SiO_2 was from 0.77 to 4.64), the TGA curve was shifted to high temperature area. It was considered that when PEG was added into silica precursor solution, these molecules can

form hydrogen bonding with Si—OH as reported by Kuraoka et al.[26] Without the available Si—OH groups, condensation reaction cannot form the bridging bonds and synthesis was halted. This molecular level's structures of gel could make the hybrid flexible. Nevertheless, the molecular level scale of PEG was resulted in decreasing the degradation temperature. On the other hand, when increasing the PEG weight fraction of the PEG solution to 40% (PEG/SiO_2 = 3.09), the diagram was obvious that thermal weight loss of the films proceed in two stages. The first weight loss stage was resulted from the molecular level scale of PEG in PEG-SiO_2 network. But with increasing the PEG rich domain which would bring micro- and/or macro- phase separation. The second weight loss stage was made by the original of entangled PEG, the crystallization behavior of PEG. The same results were reported by Chen that the homogeneous PEG-SiO_2 hybrids on a molecular level can be obtained and provided that the PEG (molecular weight = 2000) content in the hybrids was less than 30% by weight.[27]

The solvent for the PEG solution

The organic–inorganic solution was prepared by mixing the A and B which was able to choose different solvent and could further reacted and become to gel to affect the coating operation and the morphology of the films. Therefore, the gel time of organic–inorganic solution by different solvents for the B were shown that the gelation time was increased in the order of toluene < methanol < ethanol < water.
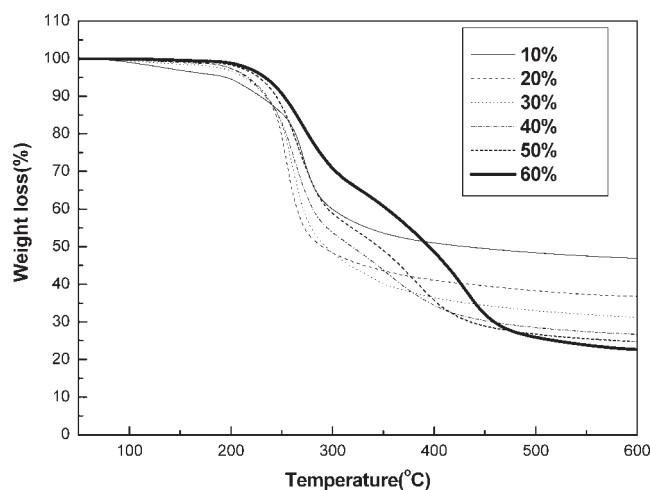

Figure 3 TGA curves of casting films prepared by different PEG weight percentage in the PEG solution. The casting solution was prepared by mixing with one weight part of silica sol precursor solution and one weight part of PEG solution.
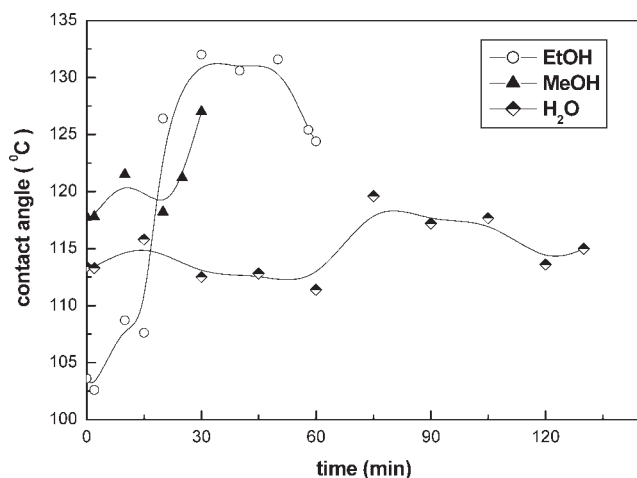
Figure 4 Effect of contact angles of the films on the reaction time of the organic–inorganic solution prepared by different solvent for PEG solution. PEG solution was prepared by dissolving 60 wt % of PEG in the solvent.

Water has the excellent polarity (polarity index is 9) among these solvents, but that of toluene (polarity index is 2.4) was the smallest one.[29] It was considered that with increasing the polarity of the solvent, the hydroxyl group in the solution was increased and the network was not easy to form. In other words, the polarity of solvent was able to decrease the opportunity of the crosslink reaction between silica precursors on each other or silica precursor with PEG that caused the gelation time increasingly. On the contrary, toluene had the weakest polarity so that the gelation time was shortest among these solvents and was not easy to be used for coating operation.

We can realize that solvent for the PEG solution could vary the gelation time of the organic–inorganic solution from above data, so the films were able to be prepared by the organic–inorganic solution with different reaction time until gel point and the results were shown in Figure 4. The result showed that the contact angles of the films were increased with increasing the reaction time of organic–inorganic solution. It was considered that with increasing reaction time of the organic–inorganic solution, the viscosity of casting solution was increased and phase separation of the PEG rich domain was easy to form. But the contact angles of the films prepared by using water as the solvent for the PEG solution was almost constant. It was considered that water had the strong polarity so that it reacted with silica sol and PEG polymer more easily than others. On the other hand, water was also evaporated slowly in the thin films so that causing the smooth surface. It was the same reason why the contact angles with time was lower than methanol and ethanol.

The reaction temperature and time of the casting solution

The reaction temperature of the organic–inorganic solution was another factor to effect the gelation time of the organic–inorganic solution. It was shown that the longest gelation time was 60 min when the temperature of the organic–inorganic solution was 19°C and the shortest gelation time was 3 min when the temperature of the organic–inorganic solution was 60°C. It was considered that with increasing the reaction temperature, the crosslink reaction was improved and the gelation time was decreased. It was inspired that the time of crosslink reaction was reduced with increasing reaction temperature. But if the formation of these ''gels'' was quickly reached that would result in difficulty of casting during coating operation. To understand the effect of the contact angles of the films on the reaction temperature of organic–inorganic solution, the films were prepared by different temperature and the results were shown that with increasing the coating temperature from 19°C to 60°C resulted in the slightly raising of the contact angles of the films. However, there was almost no obvious variation from macroscopic view. It was considered that higher coating temperature made the organic–inorganic solution more homogenous than lower one, so that intact thin films would be fabricated under higher coating temperature, but it was not the main factor to decide the surface roughness because of the less variation of the contact angles of the films prepared with different temperatures.

We can know clearly that reaction temperature can influence the gelation time from above data, but the contact angles of the thin films prepared with different reaction time under different temperature was another factor to be considered. But with increasing the reaction temperature, the gelation time was decreased. So the film prepared by lower temperatures, 19°C and 24°C, was discussed and the results were shown in Figure 5. The diagram indicated that the contact angles of the films prepared by 19°C was lower than that prepared by 24°C when the reaction time was shorter than 20 min. However, with increasing the reaction time that was longer than 20 min, the contact angles of the films prepared by 19°C was higher than that prepared by 24°C. Before 20 min, the result was the same as above statement. In the early period, the more homogenous thin films were obtained under higher temperature. But when the time was excess to 20 min, phase separation of the PEG rich domain was easy to be formed so that caused the rough surface of the films was easily to be formed under lower temperature. It was because that micro- or macro-phase separation of PEG occurred at lower reaction temperature resulted in the discontinuous rough surface that brought the higher contact angles of the as-prepared
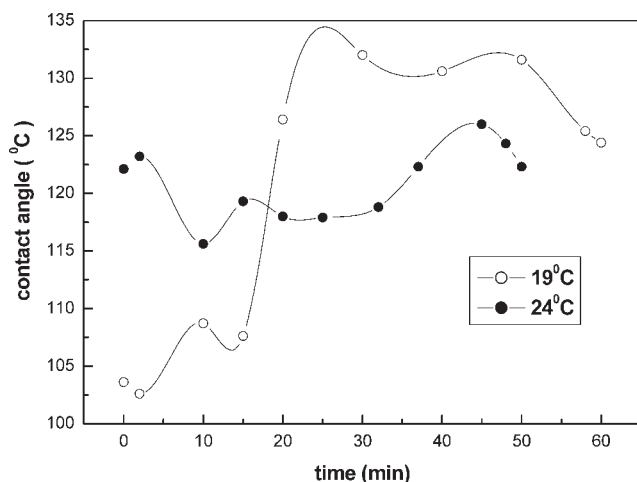
Figure 5 Effect of the contact angles of the films on the reaction time at two different reaction temperature (19°C and 24°C) of the organic–inorganic solution. The PEG solution was prepared by mixing 60 wt % of PEG in ethanol solution.

films. Spinodal demixing could result in "continuous phase" (rich phase domain) and nucleation and growth could result in "discontinuous phase" (poor phase domain), so that as-prepared films at higher reaction temperature was easy to form the smooth surface but that at lower reaction temperature was easy to form the rough surface.

Poor-solvent effect

Adding poor solvent, n-hexane, onto the thin films after the spin-coating process, was a direct method
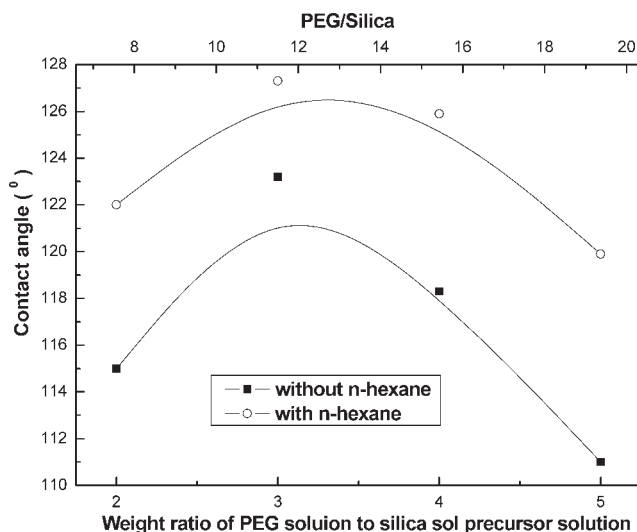

Figure 6 Effect of contact angles of the films on the ratio of silica sol precursor solution to PEG solution and the ratio of PEG to silica with adding n-hexane on the films after casting or not.

to cause phase separation on the films. It was because that the PEG polymer was precipitated immediately by adding n-hexane on the films. The effect of the contact angles of the films with introducing n-hexane after casting was shown in Figure 6. The diagram indicated that adding n-hexane onto the surface had the higher contact angles of the films. Especially, the films prepared by organic–inorganic solution in which the weight ratio of B to A was 3 (PEG/SiO$_2$ = 11.60) had higher contact angle of the film, so this ratio was chosen to follow-up experiment. From the roughness data of the films measured by AFM, the surface RMS roughness of the films prepared by without adding n-hexane on it was 39.99 nm, but that of the films prepared by adding n-hexane was 52.20 nm. Therefore, adding poorsolvent onto the surface was able to improve the roughness of the surface. It was clearly to know that adding poor solvent after the casting process indeed is to create the discontinuous phase (nucleation and growth) of phase separation on the surface, and so that caused the surface roughness.

To manufacture the superhydrophobic thin films, controlling the parameters of experimental conditions was the very important factor. First, A and B were mixed homogenously at 60°C for 2 min, it was to accelerate the crosslink reaction of the casting solution. Second, the casting solution was kept 18°C for 1 min, it was to create preliminary micro-phase separation phenomenon. Third, introducing n-hexane onto the films after casting, it was to create macro-phase separation. Finally, repeating the above procedure to have multi-layer of the films. The result was shown in Table I. It was indicated that multilayer of the films and adding n-hexane onto the films had the outstanding results. The contact angles of the films were increased with increasing the coating layer, especially adding n-hexane on each layer.

TABLE I
Contact Angles of the Films Prepared by Casting Different Coating Layer with and without Introducing n-Hexane (Poor Solvent) on the Films

No. of multilayer	Contact angle (°)		
	Without adding n-hexane	Adding n-hexane on the last layer	Adding n-hexane on each layer
1	123.2	123.2	127.3
2	131.3	140.5	137.1
3	146.6	146.7	152.0
4	149.5	150.6	157.1
5	147.6	151.2	152.7

PEG solution was prepared by dissolving 50 wt % of PEG polymer in EtOH. The organic and inorganic solution was prepared by mixing one weight part of silica solution and three weight part of PEG solution.
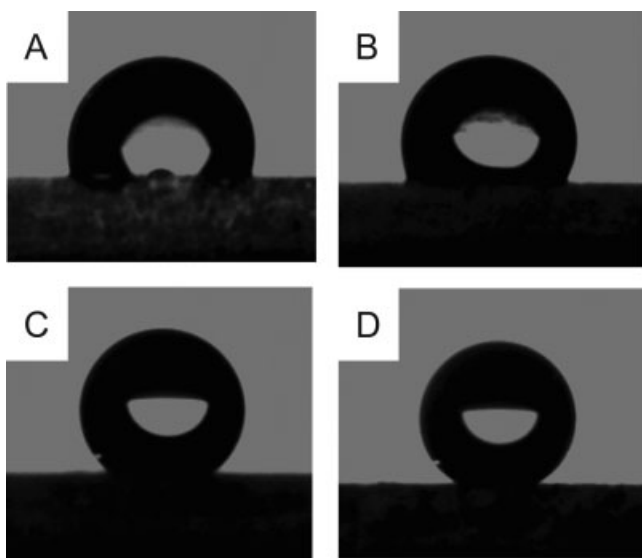
Figure 7 Pictures captured from the goniometer for a water drop on different surfaces of the films prepared by (A) one-layer without adding *n*-hexane on the layer, (B) one-layer with adding *n*-hexane on the layer, (C) four-layer without adding *n*-hexane on the layer, (D) four-layer with adding *n*-hexane on each layer. The contact angles of the films: (A) 123.2°, (B) 127.3°, (C) 149.5°, (D) 157.1°.

The water drop on different coating surfaces was shown in Figure 7. The preparation of superhydrophobic thin films has been developed by the four-layer with adding *n*-hexane on each layer. The AFM results of the as-prepared thin films was shown that the RMS roughness of four-layer of the film prepared by adding *n*-hexane on each layer was 274.9 nm but that prepared by without adding *n*-hexane on the four layers was just 172.1 nm. It revealed that introducing *n*-hexane onto the surface made the surface roughness increase. SEM micrograph of the films was shown in Figure 8. The surface of the one-layer of the film prepared by without adding *n*-hexane on the coating layer was smooth, but that of the four-layer of the films prepared by adding *n*-hexane

on the coating layer or not were roughness. The surface of the four-layer of the films without adding *n*-hexane on it exhibited a regular broken thin film, but that with adding *n*-hexane on it creating the irregular fragment and resulted in increasing the roughness of the surface.

Figure 9(A) showed that FT-IR spectra of as-prepared rough films with and without HMDS treatment, respectively. The absorption band of OH around 3500 cm^{-1} was decreased after modified surface with HMDS. The absorption band of water adsorbed on silica gel around $1500 \sim 1800$ cm^{-1} was decreased after modified surface with HMDS. From the above data, it is indicated that —OH compound was decreased modifying with HMDS. The siloxane network grew, as indicated by Si—O—Si bands at around 1050 cm^{-1} that broadened and shifted apart. The intensity of bands relating to methyl groups at 2951 cm^{-1}, which slightly increased with modification of HMDS. It revealed that hydrophobic group could bond onto the surface. The infra-red spectra information has been interpreted in detail in a previous paper.[30] However, the composition of the modified surface was studied with XPS as shown in Figure 9(B). It showed that C 1s spectrum of the rough surface treated with HMDS was observed. The single peak centered at 284.6 eV supported that modification had successfully introduced hydrophobic groups onto the rough surface.

CONCLUSIONS

Superhydrophobic silica-based thin films have been prepared by a combination of sol-gel process and adding poor solvent after casting process. The surface roughness was promoted by removing PEG4000 polymer from the films. However, the hydrophobic (methyl) group of surface was modified by HMDS. The results showed that the contact angles of the films can be controlled by the parameters of PEG weight fraction of the casting solution, solvent for
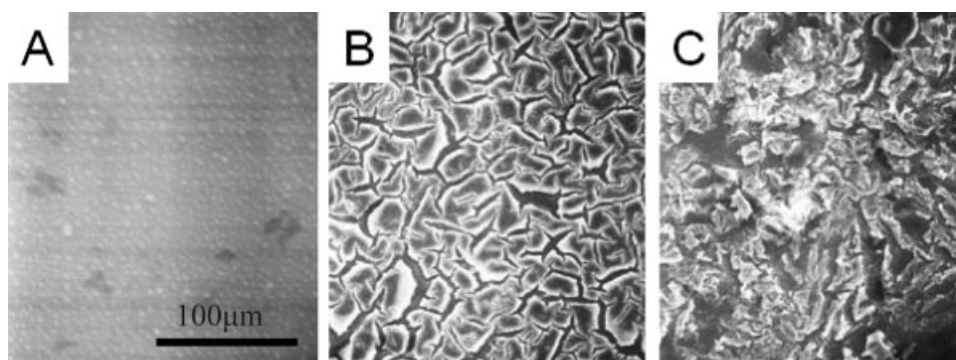

Figure 8 SEM micrographs of films prepared by: (A) one-layer without adding *n*-hexane on the layer, (B) four-layer without adding *n*-hexane on the layer, (C) four-layer with adding *n*-hexane on each layer.
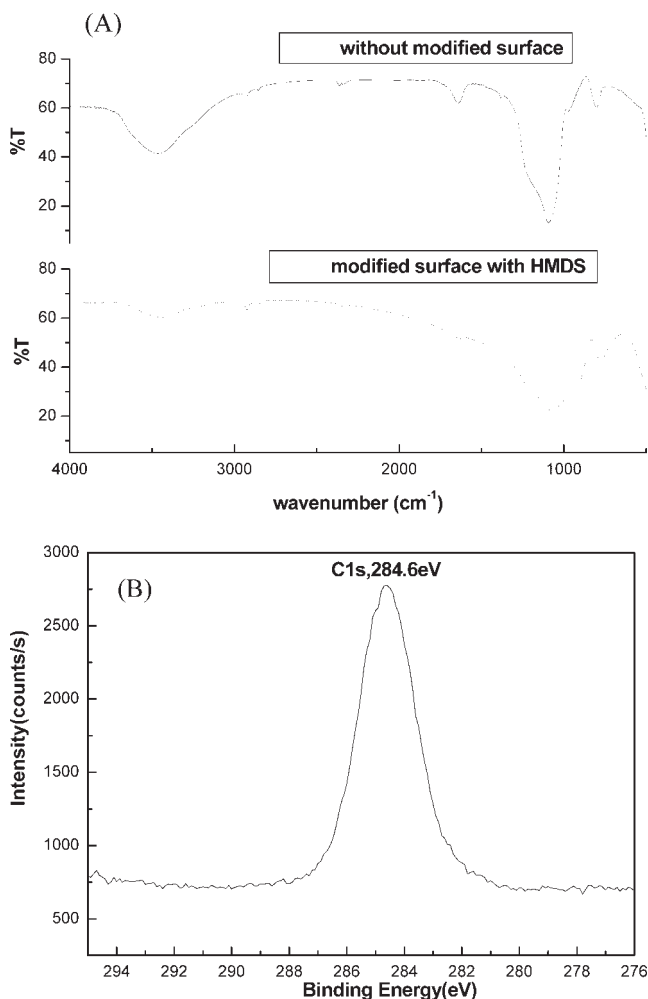
Figure 9 (A) FT-IR spectra of the films prepared with or without modification surface by using HMDS. (B) XPS spectrum of C1s of the as-prepared thin film

PEG solution, reaction temperature and time of casting solution, and introducing poor solvent on the films after casting process. Nevertheless, multilayer of the films with adding *n*-hexane onto the films during the casting process resulted in the high contact angles of the as-prepared films. The four-layer of the film with adding *n*-hexane on each layer exhibited the excellent contact angle, 157.1°. Characteristic analysis indeed is that discontinuous surface of the films can lead to the ultra-water repellent thin film.

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