

Optically transparent superhydrophobic silica-based films

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Abstract

Optically transparent superhydrophobic silica-based films were obtained by means of sol–gel processing and self-assembly (SA). Desired surface roughness was obtained by tuning the microstructures of the sol–gels through careful control of hydrolysis and condensation reactions of various silica precursors during sol–gel processing, whereas modification of surface chemistry was done by introducing a monolayer through surface condensation reaction. Such coatings were obtained by dip-coating the silica sols directly onto substrates, followed with self-assembly. The resultant silica-based coatings showed optical transparency higher than 90%, and the reflection lower than 10%, and the best advancing and receding water contact angles were found to be of approximately $165^\circ/115^\circ$. Such coatings can have applications where anti-reflection, optical transparency and superhydrophobicity are required, in addition to low temperature processing. In addition, such films can be made at room temperature involving no expensive equipment or tedious processing, and be readily coated on various substrates.

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1. Introduction

Superhydrophobic films have a wide spectrum of applications, and are used not only for resisting water and fog condensation, but also preventing contamination [1–9]. Nowadays, with the development of technology their applications have extended to some new fields, such as biocompatibility, lubricity and durability of materials, for their low free energy surface [10]. Surface wettability is described by a contact angle, which is defined by Young's equation [1,2,11–13]. For a given system, there are two basic approaches to increase the contact angle. One is to change the surface chemistry that can lower the surface energy sufficiently, which is generally referred to as the chemical method. The other is to increase the surface roughness so as to increase the true or effective surface area resulting in an increase in nominal surface energy, which is known as the geometrical method. For the formation of superhydrophobic films or coatings, modification of surface chemistry is always combined with surface roughness enhancement.

As for the chemical method, fluorine is the most effective element for lowering the surface free energy because it has a small atomic radius and the biggest electronegativity among all atoms, so it forms a stable covalent bond with carbon, resulting in a surface with low surface energy. Hare et al. [14] reported that the surface free energy increases when fluorine is replaced by other elements such as H and C, in the order $-\text{CF}_3 < -\text{CF}_2\text{H} < -\text{CF}_2- < -\text{CH}_3 < -\text{CH}_2-$, and predicted that the closest hexagonal packing of $-\text{CF}_3$ groups on the surface would give the lowest surface energy of the materials. Therefore, fluorocarbon polymer makes excellent hydrophobic films and coatings; however, the adhesion between the substrate and the fluorine-based hydrophobic coating is via van der Waals force and, thus, is very weak when such films are directly attached to substrates.

Surface roughness can also change the contact angles as the chemicals do but through a different mechanism. It is well known that water contact angles on smooth hydrophobic surfaces are generally not exceeding 120° ; contact angles of long chain hydrocarbon and fluorocarbon self-assembled monolayers are only 112° and 115° , respectively [13]. However, the situation is quite different when the surface is rough [15]. The idea is conceptually straightforward. An

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increased roughness results in an increased surface area and, thus, increased nominal or apparent surface energy. According to Young's equation, the contact angle needs to increase accordingly to balance the enlarged surface energy between the solid substrate and liquid droplet. The principle relationship between surface roughness and contact angle was developed by Wenzel [16] in 1936, and is given below [17]:

$$\cos\theta_{\text{rough}} = r\cos\theta_{\text{true}} \quad (1)$$

where θ_{rough} is the apparent contact angle of the rough surface, θ_{true} is the contact angle of a flat surface with the identical surface chemistry, and r is the ratio of actual to project surface area. Fig. 1 was plotted based on Eq. (1), which shows that contact angles on flat surfaces smaller than 90° decrease with increased roughness, while if θ_{true} is greater than 90° , θ_{rough} increases. However, Wenzel's theory is only valid when the liquid droplet has complete contact with the solid substrate over their entire mutual interface. Bieo et al. [18] modified Eq. (1), to take into account of air bubbles trapped at the interface:

$$\cos\theta_{\text{rough}} = \Phi_s(1 + \cos\theta_{\text{true}}) - 1 \quad (2)$$

where Φ_s is the fraction of the solid surface in contact with the liquid.

The effect of surface roughness on wettability, in particular, on water contact angle has been a subject of numerous studies. For example, ultrawater-repellant rough films were prepared using plasma-enhanced chemical vapor deposition of fluoroalkylsilanes [19]; expanded polytetrafluoroethylene (PTFE) vascular grafts had been treated by ion-beam etching followed by oxygen glow discharge [20]; PTFE thin films with nanometer-scale roughness were made by vacuum-deposition [21]; and rough glass plate was produced by radio frequency plasma etching and then chemi-

cally adsorbing a monolayer of a fluorocarbon compound [22]. All the methods mentioned above produce superhydrophobic surface; however, the ways for making rough surface require complicated equipment and the sample size is restricted by the size of equipment. In addition, these films are not always optically transparent, mainly due to the scattering by the relatively large particles or pores that are introduced to create desired surface roughness.

Incorporation of open porosity to a surface through wet chemical methods is one of the most effective ways to enhance surface roughness. Isotactic polypropylene (i-PP) was used to form porous films to get superhydrophobic surface with a water contact angle of 160° [23]. This type of films is simple to make with inexpensive material; however, they are optically opaque. Furthermore, adhesion of organic films to inorganic substrates is often problematic. Sol-gel-derived alumina films were also explored for superhydrophobic applications. First the sol-gel alumina films were boiled in water for 10 min to create pores (or surface roughness), and then self-assembled monolayer of fluoroalkyltrimethoxysilanes [24]. Such films have a good optical transparency >92%, good adhesion to substrates, and a large contact angle ($\sim 165^\circ$). However, while water boiling introduces porosity to the film surface, it also reduces the mechanical integrity of the film. Water boiling is also known to damage the adhesion of sol-gel films and even result in film delamination [25].

In this paper, we report our study on the formation of optically transparent and organically modified superhydrophobic silica films by sol-gel processing and self-assembly. Various surface roughness and morphology were achieved by careful control of hydrolysis and condensation reactions of selected precursors. The relationship between contact angle, surface roughness and surface chemistry was discussed. Furthermore, static contact angles and contact angle hystereses were compared and discussed. This study was intended to explore the possibility of designing and creating desired surface roughness directly through careful control of sol-gel processing, instead of optimization of both sol-gel processing and self-assembly.

2. Experiment

Five types of silica or organically modified silica sols were prepared, and referred to as sol A, sol B, sol C, sol AB and sol AC, respectively. Sol A was prepared by admixing tetraethylorthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) and methacryloxypropyltrimethoxysilane (MPS, $\text{H}_2\text{CC}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) in a molar ratio of 95:5 with HCl as a catalyst. First TEOS was partially hydrolyzed with a deficient amount of water and HCl in a solution with a molar ratio of TEOS/MPS/EtOH/ H_2O /HCl of 0.95:0.05:3.8:1:1.2 $\times 10^{-3}$ stirring at 60°C for 90 min. Then more water and HCl were added into the solution so that hydrolysis and condensation reactions could proceed further at 60°C for another 30 min. The

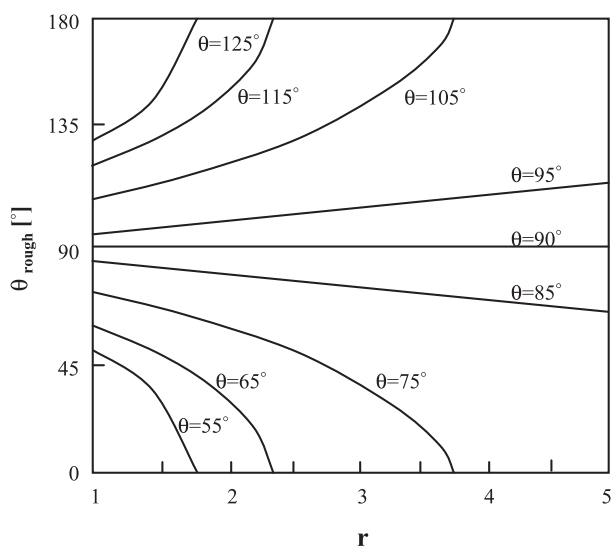


Fig. 1. The apparent contact angle as a function of surface roughness.

final sol had a molar ratio of TEOS/MPS/EtOH/H₂O/HCl of 0.95:0.05:3.8:5:4.8 × 10^{−3}. The method follows the same procedure as described by Chan et al. [25]. Sol A consists of linear oligomers or polymers.

Sol B was made by admixing TEOS and methyltriethoxysilane (MTES, CH₃Si(OC₂H₅)₃) in a molar ratio of 1:1 with NH₄OH as a catalyst. First the mixture of TEOS, MTES, ethanol, H₂O and HCl was stirred at 60 °C for 90 min to get stable sol, and the molar ratio of TEOS/MTES/ethanol/H₂O/HCl is 1:1:7.6:2.2:1.4 × 10^{−3}. Then NH₄OH (30% in water) and more water were added into the sol to adjust the pH value to 8–9, and the sol was stirred for further 15 min. The Si/H₂O molar ratio of sol B was kept at approximately 1:5 and the ethanol/H₂O ratio was 3:4 in the final sol. This procedure follows the same one as published previously by Cao and Tian [26]. Sol B consists of highly branched nanoclusters.

Sol C was made by mixing TEOS and ethanol with NH₄OH (30% in water) as catalyst. First 3 ml NH₄OH was added into 50 ml ethanol and was stirred vigorously at 60 °C for 30 min, then 3 ml of TEOS was added dropwise. After further 90 min of stirring, the final sol C was obtained. Such prepared sols would consist of monosized spherical silica nanoparticles of ~ 100 nm in diameter [27].

After aging for 45 min at room temperature, sol A was mixed with respective sol B and sol C in a volume ratio of 1:1 to form sol AB and sol AC. All the five sols were diluted with ethanol in a volume ratio of sol/ethanol of 1:1 prior to coating. Films AB and AC were made immediately after the mixing and diluting since their gelation time is relatively short (1–1.5 h at room temperature). Table 1 summarizes and compares the initial chemical compositions, catalysts, and pH values of these five sols. Included in this table also are the possible chemical species on the surfaces of the films resulted from these five respective sols after heat treatment at 110 °C in air.

All the films were made by dip-coating sols on respective glass substrates, using a withdrawal speed of approximately 14 cm/min. The glass substrates were cleaned in excess ethanol by sonication for 10 min and rinsed with deionized water before coating. After coating, the samples were dried under ambient condition for 5 min and then heat-treated at 110 °C in air for 1 h to remove the residual

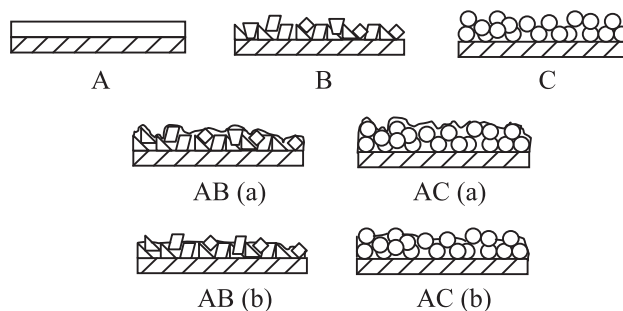


Fig. 2. Schematics of possible microstructures and surface morphologies of films A, B, C, AB and AC.

solvent. Fig. 2 shows the schematics to illustrate the possible microstructures of films A, B, C, AB and AC. Film A is derived from sol A, which consists of linear silica-based oligomer or polymer chains. Upon removal of solvent during drying, these linear oligomer or polymer chains pack to form a relatively dense and smooth film. The surface of film B is expected to be rough, since it is formed by stacking highly branched nanoclusters. The surface of film C is also expected to be rough as a result of packing of monosized silica. In film AB, nanoclusters may be embedded inside a relatively dense matrix either completely (Fig. 2AB (a)) or partially (Fig. 2AB (b)). The same possibilities exist in film AC. Both films AB and AC are expected to be rough in surface.

The surface chemistry of all films was modified with self-assembly monolayer (SAM). There are two types of SAM precursor solutions used for self-assembly. One is the solution of chlorotrimethylsilane (CTMS, (CH₃)₃SiCl), which contains –CH₃ groups and the other is tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (TFCS, CF₃(CF₂)₅(CH₂)₂(CH₃)₂SiCl) with –CF₃ groups. SAMs of CTMS and TFCS both form covalent chemical bonds with the substrate surface, although precursors containing these two groups are easily adsorbed onto any hydroxylated solid surfaces through covalent bonds, hydrogen bonds and van der Waals forces [28–30]. Prior to self-assembly, half of sol–gel-derived films were subjected to oxygen plasma etching (100 mbar), and immediately followed with submerging into DI-H₂O, so as to hydroxylate the surface. CTMS solution was prepared by dissolving CTMS in hexane and the concentration of it was 0.2 M. TFCS solution was made by the same method, but the concentration was 0.1 M because of its long fluorocarbon chains. Fig. 3 is the schematic of SAM, in which (a) shows the surface of film with CTMS monolayer, and (b) is the schematic with TFCS monolayer. The self-assembly (SA) time of these two solutions is different since the reaction rate is various. SA time of CTMS is 1 h but that of TFCS is 6 h since longer fluorocarbon chains made the reaction slower. After SA, the samples were sonicated in ethanol for 5 min to get rid of the excess CTMS or TFCS.

Table 1
Comparison of chemical composition and resulting surface structure of five silica-based sols

Sols	Composition	Catalyst	pH value	Surface bonds after heating at 110 °C
Sol A	TEOS, MPS	HCl	2	Si–O, Si–OH
Sol B	TEOS, MPS, MTES	HCl, NH ₄ OH	6	Si–O, Si–CH ₃ , Si–OH
Sol C	TEOS	NH ₄ OH	10	Si–O, Si–OH
Sol AB	TEOS, MPS, MTES	HCl, NH ₄ OH	5	Si–O, Si–CH ₃ , Si–OH
Sol AC	TEOS, MPS	HCl, NH ₄ OH	7	Si–O, Si–OH

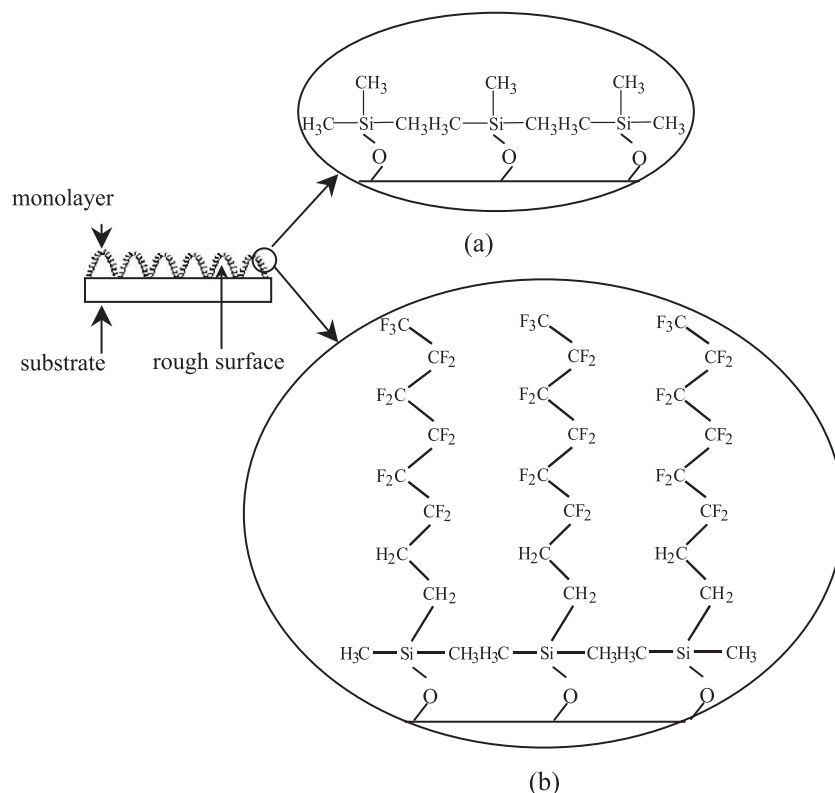


Fig. 3. Schematic of surface chemistry after self-assembly with (a) CTMS and (b) TFCS.

Surface morphologies including surface area and roughness were characterized by atomic force microscopy (AFM, Digital Nanoscope III, Veeco Metrology Group), and both of the data can be achieved from the roughness analysis of the software of AFM. Water contact angles were measured by optical microscope equipped with display camera (QX3+, Digital Blue), and manual contact angle goniometer (Model 100-00, Ramé-Hart). The optical transmittance and reflection were determined by spectrometer (PC 2000, Ocean Optics, Inc.).

3. Results and discussion

All of the films are defect-free before and after firing at 110 °C, i.e., no pinholes or cracks have been observed by means of microscopy. The films also appear smooth macroscopically and have a good optical transparency and low reflection. Fig. 4 shows the optical transmittance spectra of films A, B, C, AB and AC. The optical transmittance of all the films is higher than 90% within the wavelengths ranging from 400 to 900 nm. Transmittance of films A and B is the highest. Whereas the transmittance of films AB, AC and C is lower than that of films A and B. However, transmittance of all the five films is greater than that of bare substrate. The reason is unknown to us, but it is possible that the films with nanometer scale roughness may effectively reduce the reflection at the surface, resulting in an enhanced transmittance. Transmittance of film C is the smallest, which can be attributed to the

relatively larger silica nanoparticles (~ 100 nm in diameter) [27] and the presence of more open space (porosity) with size close to the wavelength of visible light, resulting in more scattering. The reflection of all five films is lower than that of bare substrate as shown in Fig. 5, which corroborates with the transmittance result. From this figure, we find that the difference in reflection is small among five films.

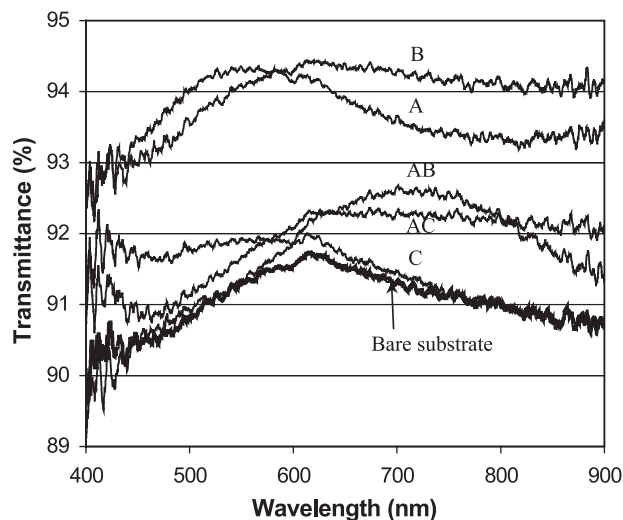


Fig. 4. Transmittance spectra of films A, B, C, AB and AC as a function of wavelength.

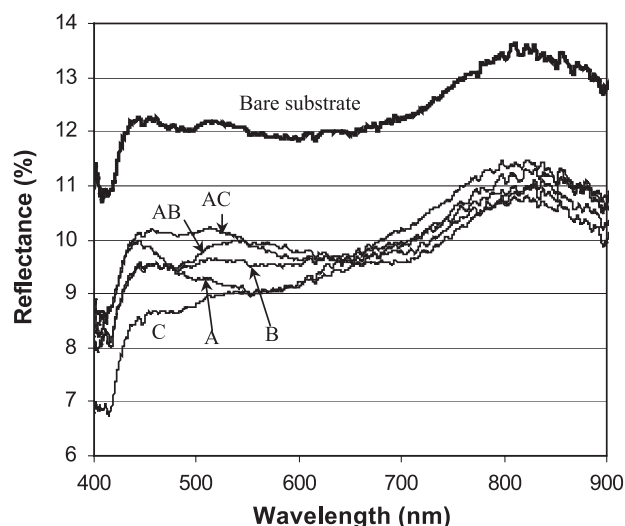


Fig. 5. Reflection spectra of films A, B, C, AB and AC as a function of wavelength.

Prior to oxygen plasma etching and self-assembly, all five films are hydrophilic with contact angles ranging from 15° (for film C) to 83° (for film B) as summarized in Table 2. The difference in hydrophilic contact angles may be attributed to both different surface roughness and chemistry. Films AB, AC, B and C are all rough, whereas film A has a smooth surface. According to Eq. (1), increased surface roughness is expected to result in a decreased contact angle when the surface is hydrophilic and the surface chemistry is identical. Films AB, AC, B and C are expected to have contact angles smaller than film A, assuming the surface chemistry is the same. However, the fact that films B and AB have greater contact angles than film A suggests that the surface chemistry is different. Thermal gravitational and differential thermal analyses (TGA/DTA) revealed that $-\text{CH}_3$ groups in hybrid silica are stable up to 400°C and subjected to oxidation or pyrolysis only at temperatures above 450°C [31]. The largest contact angle of film B is, thus, attributable to the $-\text{CH}_3$ groups that most likely reside on the surface and make film B less hydrophilic (with a larger contact angle). The relatively large contact angle of film AB suggests that the nanoclusters from sol B may only be partially embedded in the dense matrix from sol A, as described in Fig. 2AB (b), with methyl groups residing on the nanocluster surfaces. In film AC, monosized SiO_2 particles are likely to be embedded completely in the dense matrix derived from sol A (Fig. 2AC (a)) as suggested by the similar contact angles of films A and AC. However, all the difference in contact angle disappeared or became negligible when the surfaces were subjected to oxygen plasma etching for 1 min. All films became hydrophilic (with contact angles smaller than 5°), since etching is believed to remove the organic groups on the film surface as well as to hydroxylate the surface.

Table 2 also compares the static contact angles, θ_s , and the surface roughness of these five films with SAMs of

CTMS and TFCS. Both Root Mean Square (RMS) roughness and actual surface areas of all five films were obtained from AFM analyses. The RMS roughness is calculated according to the following equation:

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{av})^2}{N}} \quad (3)$$

where Z_{av} is the average height for the entire region, Z_i is the height of individual point i , and N is the number of points measured within a given area. Table 2 clearly reveals that the surface roughness increased in the order of films A, AC, AB, C and B. Film A has relatively smooth surface, whereas other films have rough surface. However, the actual surface area determined by means of AFM demonstrated a minor difference. Compared to the project surface area, the actual surface area of five films increased less than 1.02%, which is defined as the ratio of actual to project surface areas (S/S_0). As will become clear in the following discussion, such a minor increase in actual surface area cannot explain the significant enhancement of the contact angle. However, it should be noted that it is most likely that the actual surface roughness and surface area are larger than that determined by AFM, since the AFM tip used in the current study is 10 nm in diameter, comparable to the surface roughness of the films studied.

All the films self-assembled with CTMS show increased contact angles. However, only film C has the contact angle bigger than 90° , whereas all other films with CTMS assembled on the surface have contact angles less than 90° . This observation clearly suggests that no full coverage of CTMS monolayer was achieved, even after 6 h self-assembly. It should also be noticed that contact angles decrease with the roughness if the angle of the smooth surface is smaller than 90° according to Wenzel's law, as shown in Fig. 1. However, the data in Table 2 show the contact angles increased with the roughness, which implies that the formation of self-assembled monolayers was dependent of surface roughness. Surfaces with morphology changes in a small scale may be more difficult to form a full

Table 2
Comparison of roughness and static contact angles of five different films

Coatings	Surface morphology				θ_S original	θ_S after OPE (1 min)	θ_S after SA (6 h)	
	Measured		Calculated				In CTMS	In TFCS
	RMS	r	r^a	Φ_s^a				
	(nm)							
A	0.498	1	1	1	17	5	85	118
B	8.745	1.020	1.22	0.80	83	0	89	125
C	5.295	1.013	1.85	0.25	15	0	115	150
AB	4.849	1.004	1.51	0.55	65	0	89	135
AC	2.810	1.001	1.16	0.86	17	0	86	123

^a Both r and Φ_s are calculated based on the θ_s in TFCS.

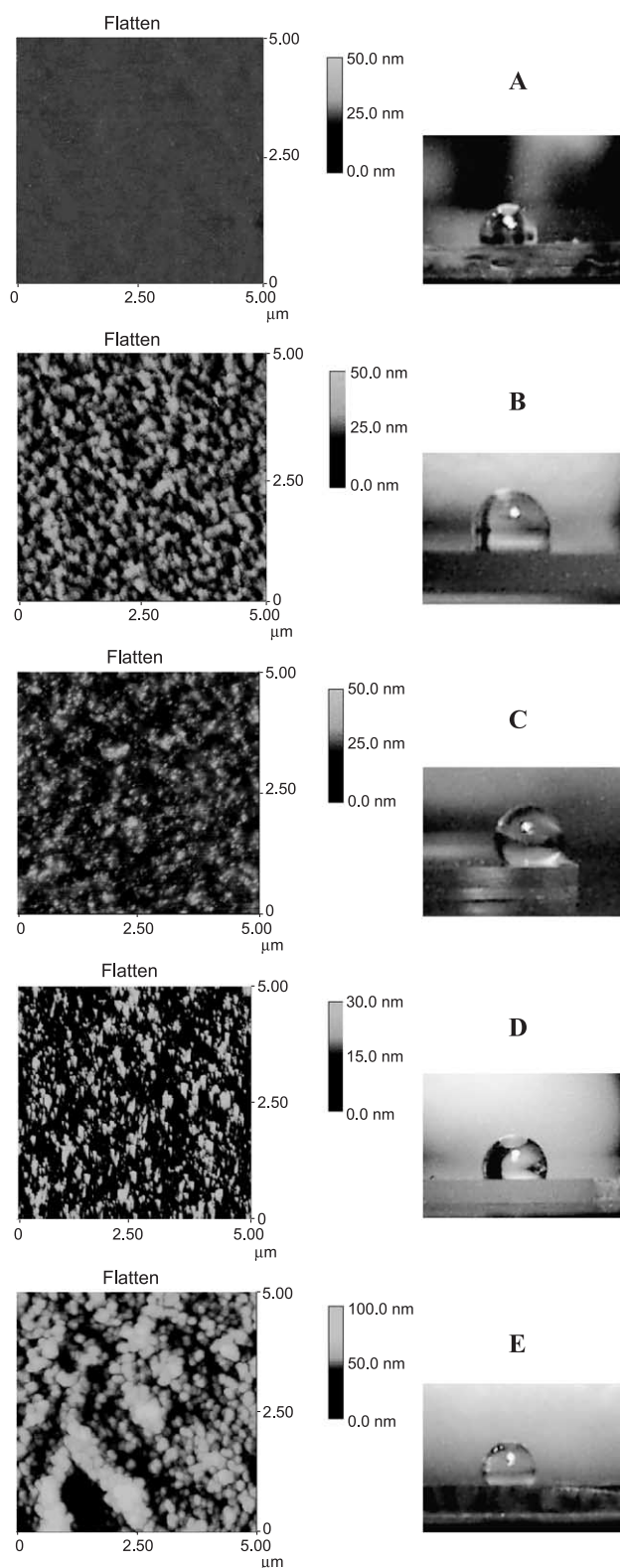


Fig. 6. AFM images and corresponding contact angle images of films, A, B, C, D, and E are film A, B, C, AB and AC, respectively. AFM images were achieved by tapping mode, scan rate of 1.001 Hz, and a scan range of $5 \times 5 \mu\text{m}$.

coverage of monolayer. Prolonged self-assembly did not result in an appreciable increase in contact angle, suggesting that full coverage of CTMS on rough surface is difficult to achieve. All five films changed from hydrophilic to hydrophobic with self-assembled TFCS monolayer on the surface. The contact angles were seen to increase with increased roughness and actual surface area. The only exception is film B with very *big* roughness, on which complete self-assembly of TFCS monolayer is very difficult, considering the long hydrocarbon chains in TFCS molecules. Contact angles and surface morphologies of these five films with TFCS monolayers are shown in Fig. 6, and A, B, C, D, E are film A, film B, film C, film AB and film AC, respectively.

A simple calculation based on Wenzel's equation revealed that the ratios of actual to projected surface area need to be 1.22, 1.85, 1.51, and 1.16 for films B, C, AB, and AC, respectively, to explain the resultant contact angles of films with TFCS monolayer measured experimentally in this study. This is in a sharp contrast with the surface ratios measured by AFM, which gave less than 1.02 for all the films. Although the resolution of AFM tip, 10 nm in diameter, may be partially responsible for possible loss of some actual surface area, such a big discrepancy may suggest that the change of contact angle may not be explained entirely by the Wenzel equation. The air trapped between the water droplets and the solid surface may play a predominant role here. The fraction of solid surface in intimate contact with water droplets was also calculated according to Eq. (2), and the results were also listed in Table 2 as Φ_s .

In Table 2, only static contact angles are listed and compared. However, a static angle does not adequately describe the hydrophobicity of films. Both the advancing (θ_A) and receding (θ_R) contact angles should be considered since the comparison between these two kinds of angles gives a clear spectrum whether the water droplets are completely unstable on a solid surface. A water droplet on a surface with a high static contact angle may remain pinned until the surface is tilted to a significant angle. The contact angle hysteresis is more important in determining hydrophobicity than the maximum achievable static contact angle [32]. The following equation describes the force

Table 3
Comparison of advancing and receding contact angles of five different films

Coatings	CA after SA (6 h)					
	In CTMS			In TFCS		
	θ_A	θ_R	F (mN/m)	θ_A	θ_R	F (mN/m)
A	100	50	59.44	125	85	48.09
B	110	65	55.69	130	95	40.06
C	125	85	48.09	165	115	39.53
AB	100	50	59.44	140	100	43.10
AC	110	65	55.69	130	95	40.46

Calculation is based on the CA in TFCS.

needed for a water droplet to start moving over a solid surface [32]:

$$F = \gamma_{LV}(\cos\theta_R - \cos\theta_A) \quad (4)$$

where F is the critical line force per unit length of the drop perimeter. The calculated values of F were listed together with both θ_R and θ_A in Table 3. It is very clear that if the difference between θ_R and θ_A is small the water drop rolls easily on the surface. The difference between θ_R and θ_A increases in the order of films C, B, AB, AC and A. The hydrophobicity of the films decreases in this same order since the critical force is increasing in this order. The critical force of film C is 6.84 mN/m, which is much smaller than that of other films, so it is the best one in hydrophobicity and agrees well with the largest static contact angle. However, the critical line force does not necessarily agree with the static contact angle. For example, for films B and AB the results are quite different. The hydrophobicity of film B is better than that of film AB, even though the static contact angle of film AB is greater than that of film B.

4. Conclusions

Optically transparent superhydrophobic silica-based films on glass substrates have been prepared by a combination of chemical and geometric approaches. Silica-based films with different roughness in the nanometer scale were made using three different sol–gel processing methods. More specifically, nanoclusters and nanoparticles were used to introduce desired nanoscale roughness. All of films have a transmittance of visible light higher than 90%. Surface modification was done by self-assembly of water repellent agents, particularly fluoroalkylsilane. The nanometer roughness was found to be good to retain the optical transparency and to reduce the surface reflection. Nanometer scale roughness was found to be too small to have an appreciable enhancement of the true surface area and prevent the formation of complete self-assembled monolayer; however, such roughness plays an essential role in trapping air between the substrate surface and the liquid droplets. The best advancing and receding contact angles were found to be of approximately $165^\circ/115^\circ$. Optimization of both sol–gel processing and self-assembly is expected to further enhance the hydrophobicity of the silica-based films.

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References

- [1] W. Chen, A.Y. Fadeev, M.C. Hsieh, D. Oner, *Langmuir* 15 (1999) 3395.
- [2] A. Nakajima, K. Hashimoto, T. Watannabe, K. Takai, G. Yamauchi, A. Fujishima, *Langmuir* 16 (2000) 7044.
- [3] A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, *Adv. Mater.* 11 (1999) 1365.
- [4] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* 12 (1996) 2125.
- [5] K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* 80 (1997) 1040.
- [6] H.J. Li, X.B. Wang, Y.L. Song, Y.Q. Liu, Q.S. Li, L. Jiang, D.B. Zhu, *Chem. J. Chin. Univ.* 22 (2001) 759 (in China).
- [7] K. Tadanaga, J. Morinaga, A. Matsuda, T. Minami, *Chem. Mater.* 12 (2000) 590.
- [8] K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* 80 (1997) 3213.
- [9] M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, *Langmuir* 16 (2000) 5754.
- [10] R.F. Brady Jr., *Nature* 368 (1994) 16.
- [11] S.Y. Yang, G.J. Hirasaki, S. Basu, R. Vaidya, *J. Pet. Sci. Eng.* 24 (1999) 63.
- [12] Y.N. Xia, D. Qin, Y.D. Yin, *Curr. Opin. Interface Sci.* 6 (2001) 54.
- [13] D.Y. Kwok, A.W. Neumann, *Adv. Colloid Interface Sci.* 81 (1999) 167.
- [14] E.F. Hare, E.G. Shafrin, W.A. Zisman, *J. Phys. Chem.* 58 (1954) 236.
- [15] S.H. Wu, *Polymer Interface and Adhesion*, Marcel Dekker Press, New York, 1982.
- [16] R.N. Wenzel, *Ind. Eng. Chem* 28 (1936) 988.
- [17] A.W. Adamson, A.P. Gast, *Physical Chemistry of Surface*, 6th ed., Wiley, New York, 1997.
- [18] J. Bieo, C. Marzolin, D. Quere, *Europhys. Lett* 47 (1999) 220.
- [19] A. Hozumi, O. Takai, *Thin Solid Films* 303 (1997) 222.
- [20] J.M. Schakenraad, I. Stokroos, H. Bartels, H.J. Busscher, *Cells Mater.* 2 (1992) 193.
- [21] J.D. Miller, S. Veeramasuneni, J. Drelich, M.R. Yalamanchili, Y. Yamauchi, *Polym. Eng. Sci.* 36 (1996) 1849.
- [22] K. Ogawa, M. Soga, Y. Takada, I. Nakayama, *Jpn. J. Appl. Phys.* 32 (1993) L614.
- [23] H. Yildirim Erbil, A. Levent Demirel, Y. Avci, M. Olcay, *Science* 299 (2003) 1377.
- [24] K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* 80 (1997) 3213.
- [25] C.M. Chan, G.Z. Cao, H. Fong, M. Sarikaya, *J. Mater. Res.* 15 (2000) 148.
- [26] G.Z. Cao, H. Tian, *J. Sol-Gel Sci. Technol.* 13 (1998) 305.
- [27] T. Pham, J.B. Jackson, N.J. Halas, T.R. Lee, *Langmuir* 18 (2002) 4915.
- [28] R. Bahulekar, N.R. Ayyangar, S. Ponrathnam, *Enzyme Microb. Technol.* 13 (1991) 858.
- [29] J.J. Chance, W.C. Purdy, *Langmuir* 13 (1997) 4487.
- [30] S.L. Ren, S.R. Yang, Q.J. Xue, *Acta Physico-Chim. Sin.* 17 (2001) 97.
- [31] S. Seraji, Y. Wu, M. Forbes, S. Limmer, T. Chou, G.Z. Cao, *Adv. Mater.* 12 (2000) 1695.
- [32] E. Wolfgram, R. Faust, in: J.F. Padday (Ed.), *Wetting, Spreading and Adhesion*, Academic Press, London, 1978, p. 213.