

F2006SC11, F2006SC12

WIPERLESS WINDSHIELDS USING LOTUS EFFECT

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KEYWORD- Superhydrophobicity, windshields, contact angle, wiper, optically transparent

ABSTRACT- *Nelumbo Nucifera* is the scientific name for the flower lotus. It has the unique property of holding water on its surface without letting it seep inside. This phenomenon is technically termed superhydrophobicity. This review paper aims to discuss the possible application of this effect in windshields to eliminate the problems pertaining to wipers. The syntheses of optically transparent superhydrophobic silica based films by different methods are discussed and the different characteristics obtained by these silica-based coatings are compared. These 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 approximately 165°/150°. The application of this concept to commercial automobile windshields is suggested.

TECHNICAL PAPER-

INTRODUCTION:

Considerable effort has been devoted to improvements of the basic performances of automobiles such as drivability, safety and environmental protection. One such area of interest has always been safety on road. The wipers in the modern automobiles create difficulties such as interfering with vision during inclement weather, proper maintenance, added weight to the car due to the components of its mechanism and aesthetically unpleasant.

The combination of various technologies such as mechanics, material science, optics results in making automobiles safer and more comfortable. Among these technologies, surface and coating technologies are utilized in several fields of application. Superhydrophobic films have a wide spectrum of applications; they are used not only for resisting water and fog condensation, but also for preventing contamination (1-9). With the development of technology their applications have extended to newer fields, such as biocompatibility, lubricity and durability of materials. (10).

To eliminate wipers we need to understand the surface and the structure of the windshield, which is, laminated glass. Surface wettability is described by contact angle, 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 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 free energy.

Surface 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 it is found 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 Waal's force and, thus, is very weak when such films are directly attached to the 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 mono layers are only 112° and 115° , respectively (13). However, the situation is quite different when the surface is rough (14). 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 (15-16), and is given by the equation,

$$\cos \theta_{\text{rough}} = r \cos \theta_{\text{true}}$$

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 projected surface area.

The effect of surface roughness on wettability, in particular on water contact angle has been a subject of interest. For example, ultrawater-repellent rough films were prepared using plasma-enhanced chemical vapour deposition of fluoroalkylsilanes (17); expanded polytetrafluoroethylene (PTFE) vascular grafts had been treated by ion-beam etching followed by oxygen glow discharge (18); PTFE thin films were made by vacuum-deposition (19); and rough glass plate was produced by radio frequency plasma etching and then chemically adsorbing a mono layer of a fluorocarbon compound (20). All methods mentioned above produce superhydrophobic surface.

In this paper we report a study on the formation of optically transparent and organically modified superhydrophobic silica based films by two important methods. The first method is 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. In the second method, super-hydrophobic thin films were prepared on glass by combining embedded nano-silica subsequent fluoroalkylsilanes coating. The

hydrophobic capability of the films depended on the concentration of nano-silica suspension. The super-hydrophobic thin film showed high transmittance in visible light wavelength. The following are the methods for the preparation of superhydrophobic surfaces.

The two methods, which have been found to be relevant and significant to the work explicated in this paper, are given in detail below.

METHOD 1:

Sol-gel processing: Three types of silica or organically modified silica are prepared and referred to as sol A., sol B, sol C. Sol A was prepared by admixing Tetraethyl orthosilicate (TEOS) and Methacryloxypropyltrimethoxysilane (MPS) in a molar ratio of 95:5 with HCl as 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/H₂O/HCl of 0.95:0.05:3.8:1:0.0012 stirring at 60°C for 90 minutes. 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 minutes. The method follows the same procedure as described by Chan et al.(21).

Sol B was made by mixing TEOS and methyl triethoxysilane (MTES) in a molar ration of 1:1 with NH₄OH as catalyst. First the mixture of TEOS, MTES, ethanol, H₂O and HCl was stirred at 60°C for 90 minutes to get stable sol. 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 further 15 minutes. This procedure follows the same one as described by Cao and Tian (22).

Sol C was made by mixing TEOS and ethanol with NH₄OH (30% in water) as catalyst. First 3ml of NH₄OH was added into 50ml ethanol and was stirred vigorously at 60°C for 30 minutes, then 3ml of TEOS was added drop wise after further 90 minute of stirring, and the final sol C was obtained.

All the 3 sols were diluted with ethanol in a volume ratio of sol-ethanol of 1:1 prior to coating. All films were made by dip coating sols on respective glass substrates. After coating the samples were dried under ambient condition for 5 minutes and then heat treated at 110°C in air for 1 hour to remove the residual solvent.

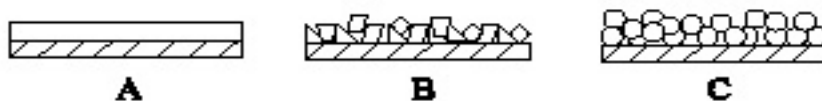


Fig 1. Schematics of possible microstructures and surface morphologies of film A, B and C.

The surface chemistry of all films was modified with self-assembly monolayer (SAM). SAMs of Chlorotrimethylsilane (CTMS) and Trideca-fluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (TFCS) both form covalent chemical bonds with the substrate surface. Prior to self-assembly half of sol-gel derived films were subjected oxygen plasma etching (100 mbar). Fig.2 is the schematic of SAM in which

(a) Shows the surface of film with CTMS monolayer, and (b) is the schematic with TFCS monolayer.

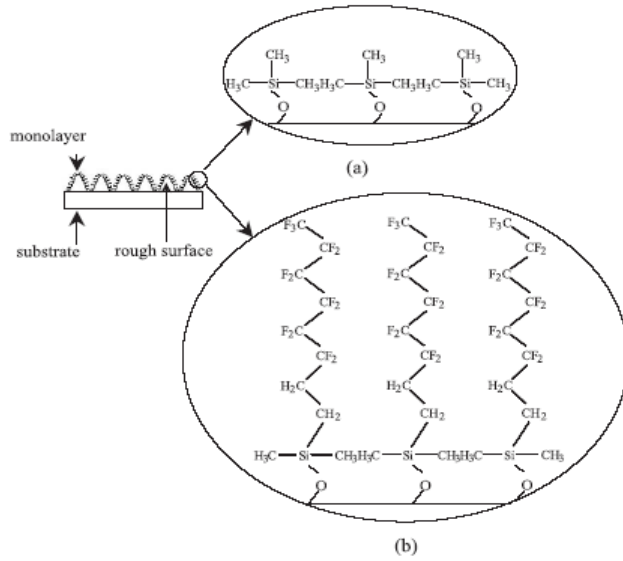


Fig 2. Schematic of surface chemistry after self-assembly with (a) CTMS and (b) TFCS.

All the films are defect-free before and after firing at 110° ie, no pinholes or cracks have been observed. The films also appear smooth macroscopically and also have a good optical transparency and low reflection. Fig 3. shows the optical transmittance spectra of films A, B,C.

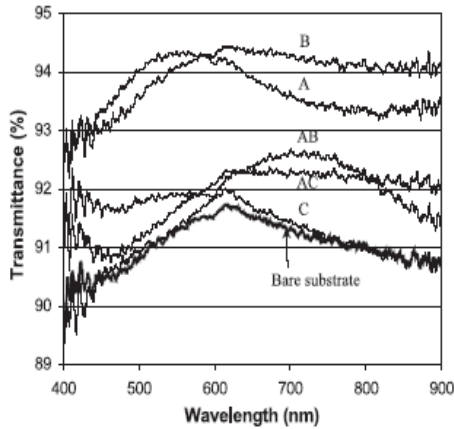


Fig 3. Transmittance spectra of film A, B, C as a function of wavelength.

The optical transmittance of all the films is higher than 90% within the wavelengths ranging from 400 to 900nm. Transmittance of film A and B is the highest whereas the transmittance of C is lower than that of A and B. However, transmittance of all the 3 films is greater than that of the bare substrate. Transmittance of film C is the smallest, which can be attributed to the relatively larger silica nano particles (~100nm in dia) (23) and the presence of more open space with size close to the wavelength of visible light resulting in more scattering.

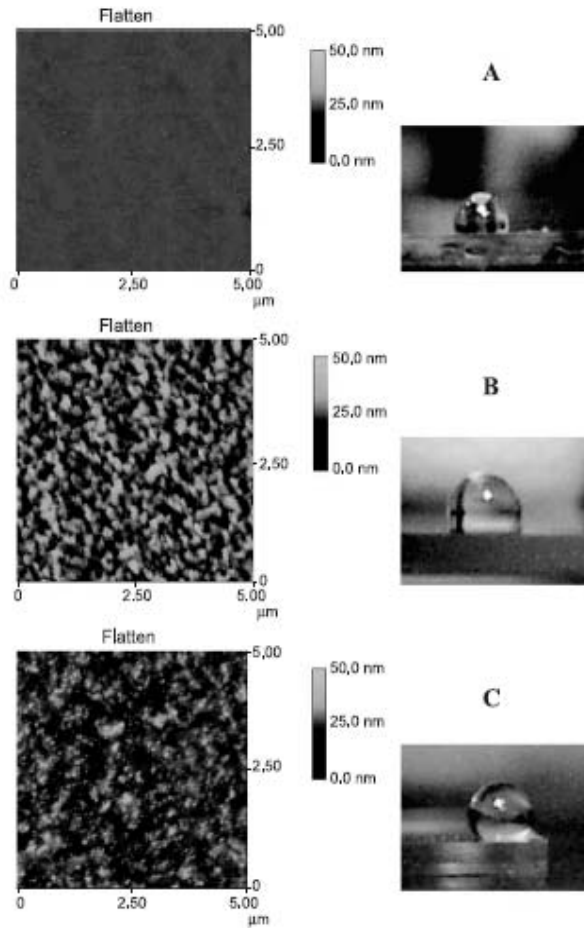


Fig 4. Images and corresponding contact angles.

The advancing (θ_a) and receding (θ_r) contact angles should be considered since the comparison between these two kinds of angles give 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 following equation describes the force needed for a water droplet to start moving over a solid surface (24).

$$F = \gamma_{lv} (\cos(\theta_r) - \cos(\theta_a))$$

where F is the critical line force per unit length of the drop perimeter. The calculated values of F are listed together with both θ_r and θ_a in Table 1.

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

Table 1. Comparison of advancing and receding contact angles.

It is very clear that the difference between θ_r and θ_a is small. The water drop rolls easily on the surface. The difference between these contact angles increases in the order of films C, B, and A. The hydrophobicity of the films decreases in the same order since the critical force is increasing in this order. The critical force of film C 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.

METHOD 2:

Superhydrophobic surface via embedding nano-silica: In this method we describe a simple way to fabricate the optically transparent superhydrophobic surface via embedding nano-silica.

The coating solution of epoxy was prepared as follows: 5.0g diglycidyl ether of bisphenol A and 1.0 g 2,5-diamino-3, 6-dimethylmercaptotoluene was dissolved in 100 g acetone. The solution of epoxy was diluted to 0.5wt% before use. The coating suspension of nano-silica was prepared as follows: 1.0 g nano-silica was suspended in 100ml ethanol, which contains 0.05wt% γ -aminopropylmethyldimethoxysilane (YDH-660). The suspension was vibrated by the ultrasonic washer for 1 hr then stirred for 2 hr at room temperature and diluted to 0.75wt%, 0.50wt%, 0.25wt% and 0.1wt% respectively.

The superhydrophobic surface was prepared as follows. The coating solution of epoxy was coated on glass that had been washed by acetone by spin coating at 1000rpm for 10 seconds and kept at room temperature and then the coating suspension of nano-silica was coated by the same way. The glass was kept at 100°C for 8 hours, and then soaked in 0.58% ethanol solution per fluoroalkyltriethoxysilane.

Concentration of nano-silica (wt.%)	Static angle (°)	Advancing angle (°)	Receding angle (°)	Hysteresis of contact angle (°)	Sliding angle (°) for 10 μ L water droplet
0	105	108	32	76	>30
0.1	110	114	40	64	>30
0.25	117	121	47	64	>30
0.5	147	158	106	52	>30
0.75	160	162	117	45	>30
1.0	168	170	151	19	11.8

Table 2. The contact angle on the surfaces of samples.

Table 2 show the static contact angles, dynamic contact angles on the surfaces of the samples and the images of water droplet on the surfaces of samples. The hydrophobic ability of samples depend on the concentration of the nano-silica suspension. The static contact angles and receding contact angles of samples increase with the increase in concentration of nano-silica because of the roughness caused by the nano-silica. The glass surface modified by the suspension of 1.08wt% of nano-silica shows the static angle as high as 168° and the sliding angle as low as 11.8° for 10-microlitre water droplets. Fig 5 shows the transmittance of the samples of light at 500nm wavelength.

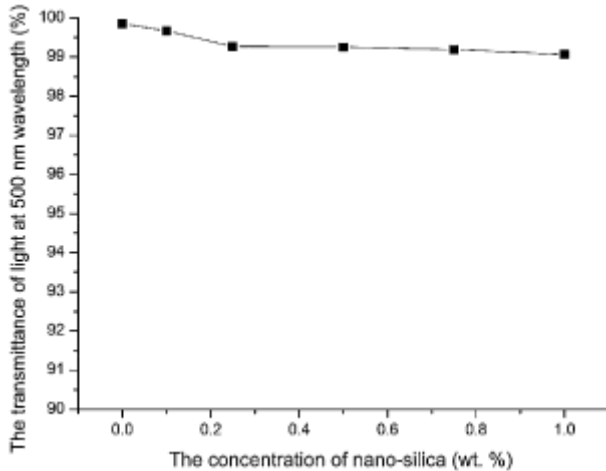


Fig 5. Shows the transmittance of light at 500nm wavelength.

The transmittance of all samples at visible light wavelengths of more than 99%. The superhydrophobic thin films show the ability to be almost transparent for visible light. Fig 6 shows the chemistry of the coating procedures as follows: First, the dimethoxysilane groups reacted with the hydroxyl groups on the nano-silica surface through dehydration reaction, show the organic tails is easy to be dissolved in ethanol. Under ultrasonic vibration, the nano-silica was surrounded by organic “tails” and then was dispersed uniformly in ethanol. Secondly, amino groups of YDH-660 can react with epoxy groups of resin coating. So, nano-silica was fixed on the glass surface (shown in fig6).

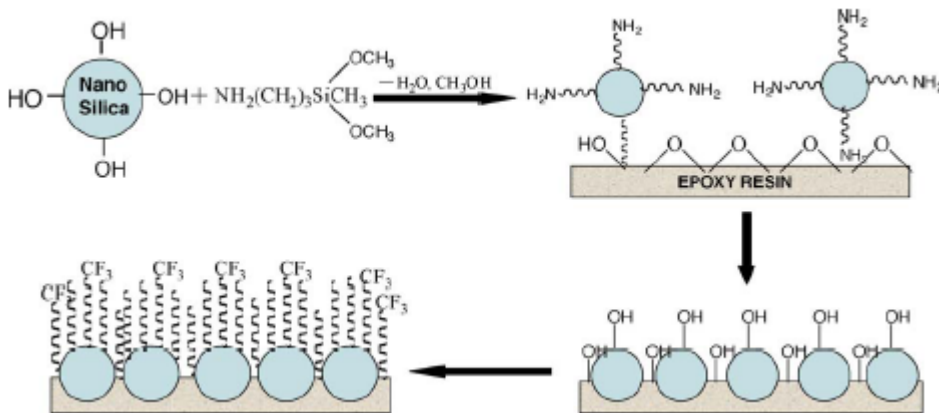


Fig 6. Shows the preparation of superhydrophobic surface.

The superhydrophobic surface has more than 99% transmittance for light at 500nm wavelength.

CONCLUSION:

Optically transparent superhydrophobic silica-based films on glass substrates have been explained by a combination of chemical and geometric approaches. All the films have a transmittance of visible light higher than 90%. Surface modification is done by self-assembly. The nanometer roughness was found to be good to retain the optical transparency and to reduce the surface reflection. The best advancing and receding

contact angles were found to be of approximately 165°/115°. The super-hydrophobic surfaces, which were prepared via embedding nano-silica, show the high transmittance for visible light and nanoscale structure. The surface has the high static contact angle of around 170°. A lucid understanding of these two methodologies will lead to applications that will eliminate the necessity of having wipers in automobiles.

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.Wantanabe, *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.
- (7) K.Tadanaga, J.Moringa, 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) S.H.Wu, *Polymer Interface and Adhesion*, Marcel Dekker Press, New York, 1982.
- (15) R.N.Wenzel, *Ind. Eng. Chem.* 28 (1936) 988.
- (16) A.W.Adamson, A.P.Gast, *Physical Chemistry of Surface*, 6th ed, Wiley, New York, 1997.
- (17) A.Hozumi, O.Takia, *Thin Solid Films* 303 (1997) 222.
- (18) J.M.Schakenraad, I.Stokroos, H.Bartels, H.J.Busscher, *Cells Mater.* 2 (1992) 193.
- (19) J.D.Miller, S. Veeramasesaneni, J.Drelich, M.R.Yalamanchilli, Y.Yamochi, *Polym. Eng. Sci.* 36 (1996) 1849.
- (20) K.Ogawa, M.Soga, Y.Takada, I.Nakaiyama, *Jpn. J. Appl. Phys.* 32 (1993) L614.
- (21) C.M.Chan, G.Z.Cao, H.Fong, M.Sarikaya, *J. Mater. Res.* 15 (2000) 148.
- (22) G.Z.Cao, H.Tian, *J. Sol Gel. Sci. Technol.* 13 (1998) 305.
- (23) T.Phan, J.B. Jackson, N.J.Halas, T.R.Lee, *Langmuir* 18 (2002) 4915.
- (24) E.Wolfram, R. Faust, in: J.F.Padday (Ed.), *Wetting, Spreading and Adhesion*, Academic Press, London,1978, p.213.