Novel transparent, liquid-repellent smooth surfaces with mechanical durability

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Abstract

A simple fabrication method for a smooth and transparent liquid-repellent film has been presented, and the smooth film was successfully obtained through sol-gel process with (3-Glycidyloxypropyl)-trimethoxysilane (GPTMS) followed by surface treatment of air plasma and fluorination. Combination of hydrolyzing of GPTMS and the surface treatment can form covalently interfacial interaction and further enhance surface robustness of the smooth film. The smooth film displays non-wetting behavior towards water and many organic liquids with very low surface tension, such as N-hexane ($\gamma_{lv}=18.4$ mN/m) and Petroleum ether ($\gamma_{lv}=17.5$ mN/m); meanwhile, optical transmittance of the smooth film is greater than 86% throughout a broad spectrum of ultraviolet and visible wavelengths. Importantly, mechanical durability of the obtained film surface was proved by tests of rubbing, wiping, thumb pressing, and peeling of adhesive tape. More surprisingly, the rubbing process can enhance surface

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1 non-wetting property and transparency of the smooth film to a certain extent. In
2 addition, the smooth surfaces can also be easily fabricated on other different metal
3 substrates. The impressive liquid-repellency of the smooth surface is concluded to be
4 governed primarily not by surface topography but rather by distribution of fluorine
5 compound on the surface.

6 **Keywords:** Liquid-repellency; Transparent; Smooth surface; Mechanical durability;
7 Surface treatment

8 **1 Introduction**

9 In actual environment, Windows, display panels, car windshields, and optical
10 equipment are constantly exposed to dirt, water, oil, and salt. These surfaces require
11 frequent cleaning to maintain high transparency, which is not only labor intensive and
12 costly, but also generate environmental waste. Conferring these surfaces with
13 self-cleaning property is a desirable way to address this challenge, and till now,
14 various research groups have tried to produce transparent superhydrophobic,
15 superoleophobic, or superamphiphobic surfaces to achieve goal [1-12]. Among them,
16 research on superoleophobic and superamphiphobic surfaces displaying
17 non-wettability of organic liquid droplets has aroused worldwide interest because of
18 its potential advantage to actual applications [7, 8, 10, 11]. For example, Seeger et al.
19 developed transparent superoleophobic surfaces by combination of versatile
20 organosilanes in a grow-from method [13]. Vollmer et al. reported a transparent
21 superamphiphobic coating using candle soot as the template [14]. However, to create
22 such surfaces, it often requires enhanced surface roughness with some special

1 structures such as re-entrant geometries or overhanging architectures [15-17], which
2 always needs a complicated process and is not easy to design. Moreover, though this
3 improved surface roughness can minimize contact area and enhance non-wetting
4 behavior, it also results in high contact pressure upon load [18, 19]. As a consequence,
5 such structured transparent surfaces are highly prone to abrasion and rapidly lose
6 self-cleaning property as a result of mechanical damage on surfaces [20-22].
7 Therefore, for practical applications, especially under outdoor environment, resistance
8 to mechanical tear and wear of the surfaces is critically important, and many aspects
9 of transparent coating with self-cleaning property have still to be explored.

10 In practical applications, it is worthwhile to note that control over the actual ease
11 of gravity-driven motion of liquid droplets down tilted surfaces is more practically
12 important than the maximum contact angles and minimum contact area between the
13 liquid and the surface. A transparent slippery surface has been fabricated via
14 liquid-infused method, which exhibited outstanding omniphobic behavior and damage
15 tolerance [23, 24]. However, such liquid-infused smooth surface is easily
16 contaminated by impurities, and unstable under rigorous conditions because of
17 evaporation or washout of the infused liquid. Surprisingly, development of smooth
18 hybrid film surfaces exhibiting exceptional dynamic dewetting behavior against
19 organic liquids has offered new approaches and practical advantages for production of
20 omniphobic coatings [25]. However, fluorinated silane was directly used as adhesive
21 on substrates, which could limit potential applications due to poor adherence of the
22 fluorinated compounds. In addition, studies on more function and mechanical

1 robustness of the films were not investigated.

2 In this work, in contrast to usual method for fabrication of non-wetting surfaces,
3 we describe a simple technique to fabricate transparent, liquid-repellent smooth films
4 derived through sol-gel process followed by surface treatment of plasma and
5 fluorination. Our strategy to design the liquid-repellent smooth films with
6 transparency and mechanical durability is shown in Fig. 1. The premise for our design
7 is that adhesion of (3-Glycidyloxypropyl)-trimethoxysilane (GPTMS) after
8 hydrolyzing can combine with the treatment of plasma and fluorination to form
9 covalently interfacial interaction between film and substrate, and further enhance
10 robustness of the liquid-repellent surface. Our smooth film displays non-wetting
11 behavior towards water and numbers of organic liquids with very low surface tension,
12 such as n-hexane (γ_{lv} =18.4 mN/m) and petroleum ether (γ_{lv} =17.5 mN/m). Optical
13 transmittance of the resulting surface is greater than 86% throughout a broad spectrum
14 of ultraviolet and visible wavelengths. Importantly, the obtained surface can keep its
15 transparency and non-wetting behavior to liquids even after many cycles of abrasion
16 tests and other mechanical tests, implying its mechanical robustness. More
17 surprisingly, abrasion process can enhance surface non-wetting behavior and
18 transparency of the smooth surface to a certain extent. This fabrication method for the
19 transparently non-wetting surface is simple and versatile, and can also be applied to a
20 wide range of substrates including glass and metals.

Fig. 1. Schematic illustration of fabrication process for liquid-repellent smooth film.

2. Experimental

2.1 Materials

(3-Glycidyloxypropyl)-trimethoxysilane (GPTMS, $C_9H_{20}O_5Si$) and 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS) were all purchased from Sigma-Aldrich. Both hydrochloric acid (HCl) and ethanol were supplied by Xilong Chemical Industry Company. Sodium hydroxide (NaOH) was purchased from Rionlon (Tianjin) Chemical Co. Ltd. Both ammonia aqueous solution (25 wt%) and acetone were provided by Kaitong Chemical Reagents Company (Tianjin). All chemicals were used directly without further purification.

2.2 Preparation of smooth GPTMS film

5 mL of GPTMS was added into 80 mL of ethanol at room temperature and stirred magnetically for 2 h. 1 mL of deionized water was then introduced into the solution, and pH of the precursory solution was adjusted to 4 with hydrochloric acid,

1 followed by stirring for 10 h, whereafter the solution was coated onto a cleaned glass
2 slide with dip-coating method, forming a thin film with thickness about 200 nm. The
3 film was heated respectively at 60°C for 24 h and at 100°C for 2 h under a relative
4 humidity of 40 %, obtaining pristine GPTMS film. After that, the pristine GPTMS
5 film was treated by air plasma at 100 W for 15min, and rapidly fluorinated by using
6 CVD technique according to our previous report [26]. The plasma treated film and an
7 open glass vessel containing about 0.1 ml of PFOTS were put in a sealed desiccator
8 under vacuum for 1 min at room temperature. Afterward, the sample was placed in a
9 vacuum oven at 80°C to remove untreated fluorosilane, and smooth GPTMS film was
10 obtained. It should be specifically noted that the obtained smooth films were rubbed at
11 certain times using a 500 g weight wrapped in filter paper before different
12 investigations, and applied pressure is about 4.7 kPa. Schematic illustration of rubbing
13 test on the smooth surface is shown in Fig. 2.

Fig. 2 Schematic illustration of the rubbing tests with a 500 g weight wrapped in filter paper.

14 2.3 Characterization

15 Surface morphology analysis of the film was investigated by both field-emission
16 scanning electron microscopy (JEOL JSM-6701F FESEM) and Atomic force

1 microscopy (AFM, Nanoscope IIIa, USA). Fourier transform infrared spectrometer
2 (FTIR, IFS66 V/S, Bruker) was used to study possible groups on the films. The
3 contact angle (CA) and contact angle hysteresis (CAH) of liquid drops on film
4 surfaces were measured with a KRÜSS DSA 100 (KRÜSS Company, Ltd., Germany)
5 apparatus by injecting 10 μ L of probing liquid onto samples. The average values of
6 CA and contact angle hysteresis (CAH) were achieved by measuring the same sample
7 at five different positions. The chemical composition information of the surface was
8 acquired by a VGESCALAB210 X-ray photoelectron spectrometer (XPS). Thickness
9 of the film was measured by Gaertner Ellipsometer (L116), and optical transparency
10 of the films in visible range was measured by UV–vis spectroscopy (Agilent
11 Technologies, Cary 60). Additionally, mechanical durabilities of the films were
12 evaluated by wiping test, thumb pressing test, and adhesive tape peeling test.

13

14 **3. Results and discussion**

15 Objective of this work is to develop a transparent and liquid-repellent smooth film
16 with mechanical durability. To achieve this, surface energy of the film needs to be
17 lower than the surface tension of all probe liquids, and chemically active fluorinated
18 binders need to be used. However, fluorinated compounds generally have poor
19 adherence and mechanical durability [11, 19]. Therefore, in this study, GPTMS was
20 selected as binder because it is known to be durable and can offer strong adhesion to
21 interface between film and substrate [27, 28]. Additionally, air plasma was carried out
22 to obtain hydroxyl groups ($-OH$) on GPTMS film surfaces, and PFOTS reacted with
23 $-OH$ to form covalent grafting of perfluoroalkyl groups on the surfaces via chemical

1 vapor deposition (CVD).

Fig. 3 (a) CAs and CAHs of acetone droplets as a function of thickness for the smooth GPTMS films; (b-d) the slippage process of an acetone droplet (10 µL) on the smooth film with thickness of about 190 nm.

2 For understanding of influence of film thickness on surface wettability of the
3 smooth GPTMS film, liquid-repellent behavior of acetone droplet on the surface was
4 tested for samples with different film thickness. In Fig. 3a, no obvious change in the
5 liquid-repellent behavior of the surfaces with different film thickness is observed, and
6 the surface with thickness of about 190 nm shows a relatively low CAH of 9.7°.
7 Meanwhile, it can be found that CAs of acetone droplets on the surfaces are all below
8 46°, which is different from traditional non-wetting textured surfaces with Cassie state
9 features (CAs of liquid droplets are above 150°) [29]. CAH of liquid droplet is the key
10 factor for the smooth surface in this work, due to low CAH is more practically
11 important than CA for liquid-repellent materials in real application. As shown in Fig.
12 3 b-d, in a very short period of time (only 0.44 s), the acetone droplet on the smooth
13 surface can rapidly slide off, exhibiting remarkable liquid-repellent property.

Fig.4 Changes in values of CAs and CAHs of the acetone droplets (10 μ L) on the smooth GPTMS film at different rubbing times.

1 In order to reduce roughness of the GPTMS films and further research their
2 wear-resistant, the rubbing method was carried out, and the samples were rubbed at
3 different times using a 500 g weight wrapped in filter paper before investigations.
4 Surprisingly, CAHs of acetone droplets on the smooth surfaces decrease with rubbing
5 times in the range of 0-50, and CAHs are always below the value of 10° even though
6 the rub times are over 50; meanwhile, CAs of acetone droplets keep in the range of
7 44-50°(Fig.4). Therefore, in addition to special explanation, the smooth GPTMS films
8 in this work are all rubbed at 50 times, which possess the low CAH value of 6.9°.The
9 above observation can further confirm wear-resistant of the smooth surface to a
10 certain degree.

Fig.5 FESEM images (a and b), AFM topography image (c) of the pristine GPTMS film. FTIR

spectrum (d) of the pristine GPTMS film and after further fluorination.

Fig. 5a and b show FESEM images of the smooth GPTMS film, exhibiting a homogenous and uniform surface over glass substrate. The smooth feature can be also seen from AFM image in Figure 5c, in which average root-mean-square (Rrms) roughness of the film surface was calculated to be only 0.816 nm over an area of $5 \times 5 \mu\text{m}^2$. As shown in Fig. 5d, Si-OH and Si-O-Si groups formed during the hydrolyzing and condensation reaction could get covalently bonded with the glass substrate by formation of Si-O-Si bonds, and the presence of the band at 1244cm^{-1} is attributed to C-F stretching vibration, which demonstrates that the fluorinated group was successfully grafted on the silica surface.

Fig.6 FESEM images of the GPTMS films before (a) and after air plasma treatment (b) and after further CVD treatment with PFOTS (c); (d), (e) and (f) are the magnified images of (a), (b) and (c), respectively.

1 For further study of influence of the treatments on surface morphology of the
2 smooth GPTMS film, FESEM images of the film surface before and after air plasma
3 treatment, and after further fluorination are shown in Fig.6. Compared with the
4 pristine GPTMS film (Fig.6a, d), the film surface after air plasma treatment (Fig.6b, e)
5 became obviously rougher, on which some nanoparticles appeared due to etching of
6 the air plasma. However, after further fluorination, surface roughness was slightly
7 decreased due to a covering of fluorine compound, as shown in Fig.6 b, e. A similar
8 phenomenon can be also found that surface of the pristine GPTMS film become much
9 flatter after only CVD treatment with PFOTS (see Fig. S1).

Fig.7 XPS survey spectra of GPTMS film before and after different surface treatments.

1

2 **Table 1** Atomic concentration (%) of GPTMS films before and after surface treatment

Sample	F (at. %)	O (at. %)	C (at. %)	Si (at. %)
The pristine GPTMS film	--	9.29	72.61	17.67
After air plasma treatment	--	55.57	14.5	26.94
After further fluorination	27.53	37.9	14.27	20.29

3 In order to have a better understanding about formation of the smooth GPTMS film,
4 XPS characterization was also carried out. Fig.7 shows XPS survey spectra of the
5 smooth film before and after deferent surface treatments, in which peak intensity of C
6 on the film surface decreased greatly after the air plasma treatment and fluorination,
7 successively. After further fluorination, as listed in Table 1, the atomic concentration
8 of C was reduced from 72.61 % to 14.27 %, and F and O became two major elements
9 on the surface, the atomic concentrations of which were 27.53 % and 37.9 %,

1 respectively. These obvious changes of the prominent peaks in Fig.7 further confirm
 2 the successful functionalization on the smooth surface, which lessen surface energy
 3 and deduce surface liquid-repellency [19]. In addition to this, the liquid-repellent
 4 behaviors of the film surfaces before and after surface treatment are also shown in Fig.
 5 S2, acetone droplet can easily slide off the surface after air plasma and fluorination,
 6 especially after rubbing treatment, slipping time of the liquid droplet can be obviously
 7 shortened.

Fig.8 FESEM images of the smooth GPTMS films after rubbing at 10 times (a), 30 times (b), 50 times (c) and 100 times (d), respectively. (e), (f), (g) and (h) are the magnified images of (a), (b), (c) and (d), respectively.

8
 9 Rubbing test is an important and practical approach to investigate the mechanical
 10 durability of the smooth GPTMS films, and effects of the rubbing times on surface
 11 morphology of the smooth film are shown in Fig.8. After rubbing at 10 times (Fig.8 a
 12 and e), small reduction of surface roughness on the smooth GPTMS film was taken
 13 place as compared to the surface without rubbing (Fig. 6c and f). Subsequently, it can
 14 be clearly seen that reduction of surface roughness is obvious and the surface is much

1 flat after more rubbing times. However, after rubbing at 100 times, small increase of
2 surface roughness appeared on the smooth surface in Fig.8d and h. The phenomena
3 can be also revealed in the AFM images of the smooth surface after different rubbing
4 times (Fig. S3), and it can be observed that the surface roughness of the film without
5 rubbing and after rubbing at 50 times is 1.953 nm and 0.784 nm, respectively;
6 meanwhile, the surface roughness increase to 1.073 nm as the smooth surface was
7 rubbed at 100 times. In our present case, CAHs of acetone droplets on the smooth
8 surface changed with the rubbing times, and excellent liquid-repellent behavior could
9 be achieved when the smooth surface was rubbed at 50 times (Fig.4).

10 In conventional rough omniphobic surfaces, hierarchical structures and fluorine
11 concentration play the key roles to obtain liquid-repellent performance toward probe
12 liquids [18]; therefore, fluorine concentration of the smooth GPTMS film surface after
13 rubbing at different times were investigated. As clearly seen in Table S1, fluorine
14 concentration of the surfaces reduced from 27.53 % (without rubbing) to 15.65 %
15 (rubbing at 100 times), and that of the surface rubbed at 50 times is 16.90 %.
16 Corresponding to the results from Fig.4, it could be further inferred that CAHs of
17 acetone droplets are not closely associated with higher fluorine concentration on the
18 smooth surfaces. Such a trend has not been observed frequently in the conventional
19 rough omniphobic surfaces.

20 Actually, judging from the above results, the outermost surface of the smooth
21 GPTMS film is mainly covered by silanol and perfluoroalkyl groups after the
22 treatment of plasma and fluorination. In addition, the surface energy of smooth film

1 was calculated to be 10.5 mN m^{-1} by using three liquids method. Packing density of
 2 the perfluoroalkyl groups on the surfaces could be gradually reduced with the
 3 increasing rubbing times; meanwhile, physical mobility of the neighboring
 4 perfluoroalkyl groups might be enhanced, meaning liquid droplets in contact with
 5 them can experience very low energy barriers between metastable states, leading to
 6 formation of excellent liquid-repellent surface [25, 30]. Additionally, when the
 7 surface was rubbed at overfull times, more silanol groups could expose on the surface
 8 and further weaken the liquid-repellency. Thus, we can further conclude that the
 9 impressive liquid-repellency of the smooth film surface is attributed to be governed
 10 primarily not by surface topography but rather by fluorine compound on the surface.
 11 Moreover, higher amount of long perfluoroalkyl groups alone cannot offer such good
 12 liquid-repellency, and distribution of the perfluoroalkyl groups on the smooth surface
 13 should be the key factor.

Fig. 9 (a) Transmittance spectra of the smooth GPTMS films on glass slides after rubbing at different times, inset: photographs of bare glass slide and smooth surface; (b) Transmittance spectra in the wavelength range of 500-600 nm.

14 For omniphobic surfaces, good light transmission can make them useful in many

1 practical applications, such as windows and optical equipment. UV-vis spectra (in
2 transmittance mode) of bare glass slide and the smooth GPTMS films after different
3 rubbing times were investigated and shown in Fig. 9. It is clearly observed that
4 transparency of the smooth surfaces can be improved with increasing rubbing times.
5 The maximum transmittance of the smooth surfaces reaches as high as 90.5% at
6 wavelength of 545 nm (Fig. 9b). In contrast to the transmittance of bare glass slide
7 (90.7%), the average transmittance of the smooth surfaces is greater than 86 % in the
8 wavelength range of 400–800 nm, Optical transparency of the smooth surface is
9 highlighted in Fig. 9 inset, which shows that letters can be visible underneath the
10 coated glass slide. In addition, the liquid-repellency of the smooth surface is
11 particularly highlighted in Table S2 and MovieS1, which shows that liquid-droplets
12 with different surface tension (such as hexadecane and n-hexane) can easily slide off
13 the surface. It is worth noting here that water droplet on the smooth surface shows
14 higher CAHs (21.8°) in contrast with other organic liquid droplets, which is probably
15 attributed to that high dielectric constant of water can cause liquid-film interface to
16 increase surface energy and further affect non-wetting behavior of the water [31].
17 Further work and improvement on the phenomenon need to be explored in the future.

18 Subsequently, mechanical durability of the smooth liquid-repellent surfaces was
19 proved through the tests of anti-wiping, anti-touch, and anti-peeling of adhesive tape,
20 and results are shown in Fig.10 and Movie S2. Wiping test was performed with a
21 piece of polyester fabric, and no visible decrease of non-wetting behavior of the
22 surface can be observed after several wiping times. The acetone droplet can still easily

1 slide off the smooth surface after pressing the surface with thumb, displaying obvious
2 liquid-repellency. The similar results can be also found on the smooth surface after
3 peeling test with adhesive tape, which can further prove the mechanical durability of
4 our smooth films.

Fig. 10 (a) Wiping test with polyester fabric, (b) pressing test with thumb, (c) peeling test of
adhesive tape.

5 We have also coated the smooth GPTMS films on Aluminum and Titanium alloy
6 to investigate the liquid-repellent properties (Fig. S4). It is observed that the film
7 surface could remain stable and exhibit liquid-repellent properties irrespective of the
8 type and nature of the substrate over which it was coated. Hence, we believe that the
9 smooth GPTMS films in present work may be suitable for industrial and commercial
10 applications as well.

11 **4. Conclusions**

12 In summary, we have presented a simple fabrication method for a smooth and
13 transparent liquid-repellent film which was successfully derived through sol-gel
14 process with (3-Glycidyloxypropyl)-trimethoxysilane (GPTMS) followed by surface
15 treatment of air plasma and fluorination. The hydrolyzing of GPTMS and the surface
16 treatment can form covalently interfacial interaction at film/substrate interface and
17 film/ fluorinated compound interface, and further enhance robustness of the smooth

1 film surface. The smooth film surface displays liquid-repellent behavior towards
2 water and numbers of organic liquids with very low surface tension; meanwhile, the
3 optical transmittance of the resulting surface is greater than 86% throughout a broad
4 spectrum of ultraviolet and visible wavelengths. Importantly, the smooth surface can
5 retain its transparency and liquid-repellency even after many cycles of rubbing tests
6 with a 500 g weight wrapped in filter paper, exhibiting its mechanical robustness.
7 More surprisingly, the rubbing process can enhance the surface liquid-repellent
8 property to a certain extent. Moreover, the mechanical durability of the smooth
9 surface was further proved through the tests of anti-wiping, anti-pressing, and
10 anti-peeling of adhesive tape. According to our experimental results, we can conclude
11 that the impressive liquid-repellency of the smooth surface is governed primarily not
12 by surface topography but rather by distribution of fluorine compound on the surface.
13 In addition, the smooth liquid-repellent surface can also be easily fabricated on other
14 different metal substrates. This study represents an important and facile way to the
15 fabrication of transparent liquid-repellent materials with mechanical durability, and
16 could be promising in a variety of practical applications.

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Graphical Abstract

A smooth and transparent liquid-repellent film with mechanical durability was fabricated by a facile approach

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