Chemical Engineering Journal 246 (2014) 254-259

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Short communication

Anti-fingerprint properties of non-fluorinated organosiloxane self-assembled monolayer-coated glass surfaces



Chemical Enaineerina

Journal

Ampornphan Siriviriyanun^a, Toyoko Imae^{a,b,*}

^a Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 10607, Taiwan, ROC ^b Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 10607, Taiwan, ROC

HIGHLIGHTS

- Trimethoxymethylsilane and its hybrid possess anti-fingerprint property.
- Anti-fingerprint property can be evaluated by contact angle of oleic acid.
- Molecules with anti-fingerprint property have amphiphobicity property.

G R A P H I C A L A B S T R A C T

Moderately amphiphobic non-fluorinated trimethoxymethylsilane and its hybrid with oleophilic octadecyltrimethoxysilane possessed anti-fingerprint property comparable to fluorinated compounds.



ARTICLE INFO

Article history: Received 7 December 2013 Received in revised form 19 February 2014 Accepted 21 February 2014 Available online 3 March 2014

Keywords:

Self-assembled monolayer Non-fluorinated organosiloxane Amphiphobicity Anti-fingerprint property Oleic acid

ABSTRACT

Self-assembled monolayers of organosiloxanes and their hybrids with different functionalities were successfully fabricated on glass surfaces by sol-gel technique. Contact angles with water and hexadecane revealed that the examined organosiloxanes can be classified into hydrophobic/oleophilic and hydrophobic/oleophobic molecules, and the latter character can be called amphiphobic. Since contact angles of amphiphobic oleic acid, a main component of finger print, is high for amphiphobic organosiloxanes, it can be revealed that anti-fingerprint property is strictly involved in amphiphobicity and evaluated by contact angle of oleic acid. Moderately amphiphobic non-fluorinated trimethoxymethylsilane and its hybrid with oleophilic octadecyltrimethoxysilane possessed anti-fingerprint property comparable to fluorinated compounds. In these cases, the roughness of glass surfaces may not necessarily influence in the anti-fingerprint property.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, touch screen displays are common in devices such as smart phones and tablet computers; however, fingerprint easily sticks to the display and makes it look dirty. Therefore, the fingerprint problem on the touch screen surface is a most pressing issue to be solved by the development of the protective coating materials, which possess hydrophobic and oleophobic (i.e. amphiphobic) properties. The amphiphobic (water and oil repellent) property can be achieved by the construction of the morphological structure with reentrant curvature in combination with the chemical composition and roughness on surfaces [1–6]. This character is derived from a



^{*} Corresponding author. Address: Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan ROC.

E-mail address: imae@mail.ntust.edu.tw (T. Imae).

nanoscaled concave structure consisting of cavities, in which the capillary force produced at the liquid–air interface inside the reentrant is able to repel liquid (water or oil) entering in the void [3,7].

Organosiloxanes can react with inorganic substrates such as glass through the formation of siloxane (Si–O–Si) bonds and provide functionality (e.g. alkyl, fluorinated and etc.) on the substrates [8]. Such functionalization can alter the properties of the substrate surfaces. Thus, the fabrication of self-assembled monolayers (SAMs) organosiloxanes with an appropriate functionality by the sol–gel method might be a facile, effective technique for coating various kinds of substrates by thin films, especially, to apply amphiphobic property on the surfaces. In addition, it does not need specific equipment and aggressive conditions. Moreover, since the thickness of SAM is on the nanometer scale, the visual appearance of the surface might not be affected by the SAM formation on it [9,10].

In the present work, a simple approach was provided to construct the amphiphobic property on glass surface. Organosiloxanes with various kinds of organic functionalities were fabricated on the glass surface through the sol-gel method. The hydrophobic and oleophobic properties of organosiloxane SAMs were investigated by contact angle measurements of droplets of water and n-hexadecane, respectively. The contact angle of oleic acid was also measured to evaluate the anti-fingerprint property on the modified glass surfaces, since oleic acid is a main component of fingerprint [11]. Moreover, the surface morphology or roughness of the modified glasses was investigated by an atomic force microscopy (AFM). The anti-fingerprint property was assessed in connection with the amphiphobic property and roughness of these ultrathin organic films.

2. Experimental

2.1. Modification of glass surface by SAMs of organosiloxanes

A SAM of organosiloxane on glass was prepared as shown in Scheme 1. The glass substrate was immersed into a piranha solution (H₂SO₄: H₂O₂ = 3:1) for 30 min to clean and create hydroxyl groups on the glass surface, and then the glass was rinsed with water several times. An aqueous solution of organosiloxane (2 v/ v%) was prepared by mixing organosiloxane with water, ethanol (10 v/v%) and 0.1 M HCl (3.3 v/v%) and by adjusting pH of the solution to 3.5 for hydrolyzing organosiloxane for 1.5 h at room temperature. Then the clean glass substrate was dipped into the solution of hydrolyzed organosiloxane, and the solution was stirred for 24 h at room temperature. The obtained siloxane SAM-coated glass substrate was washed with ethanol to remove unreacted chemicals and dried overnight in an oven at 110 °C.

3. Results and discussion

SAMs of organosiloxanes with different organic functions such as hydrophilic, hydrophobic, phenyl and fluorinated moieties as summarized in Table 1 were prepared on glass surface by the sol-gel method (Supplementary Fig. S1). The formation of organosiloxane SAM on glass surface [12–14] was confirmed by water contact angle, as shown in Fig. 1 and Table 2. After organosiloxane SAMs were fabricated on the glass surface; the water contact angles were remarkably increased, depending on the organic moiety of siloxanes, as summarized in Table 2. The results indicate that surfaces become hydrophobic in the order of hydrophilic moiety < phenyl moiety \leq fluorinated moiety. In addition, the hydrophobicity of siloxane with hydrophobic moiety depends on the organic moieties, although the difference of water contact angles is not so large (74°–92°).

For evaluation of the oleophobic property, n-hexadecane was used as a probe liquid. It was observed that APTES- and GPS-treated glass surfaces exhibited high oleophilicity as well as a hydrophobic ODS-treated surface, since these surfaces were well wetted by hexadecane, being coincided with the result that the water contact angle was relatively in the same range as on the SAM with hydrophobic terminal moiety. Even though APTES- and GPS-treated glass surfaces have hydrophilic terminal moiety, it is possible that amine terminal of APTES comes close to the hydrophilic glass surface to form hydrogen bonding with hydroxyl group on it and then hydrophobic propyl group is exposed on the modified glass surface [15]. For the case of GPS-glass, the ring opening of epoxy group by acid-catalyzed polymerization easily occurs. The polymeric network can be then formed and the hydrophobic alkyl group is exposed on glass surface [16]. The observed values of hexadecane contact angle mentioned that the oleophobicity of phenyl-SAM glass was almost same as that of bare glass and fluorinated-SAM glass was rather oleophobic. It must be remarked that the order of oleophobicity in hydrophilic moiety < phenyl moiety < fluorinated moiety is same as that of hydrophobicity from water contact angle, indicating the increase of amphiphobicity in this order. The oil-repellency of SAMs with hydrophobic moiety depended on the chemical structure, although it was independent of the variation of the hydrophobicity from water contact angle.

Table 1	
i abic i	

List of organosiloxanes	with	different	functionalities

_		
	Functionality	Organooxysilane
	(1) Hydrophilic	(1.1) 3-Aminopropyltriethoxysilane (APTES) (1.2) 3-Glycidoxypropyl trimethoxysilane (GPS)
	(2) Hydrophobic	(2.1) Trimethoxymethylsilane (TMS)(2.2) Isobutyl(trimethoxy)silane (ITMS)(2.3) Tetraethyl orthosilicate (TEOS)(2.4) Octadecyltrimethoxysilane (ODS)
	(3) Phenyl	(3.1) Phenyl (trimethoxyphenylsilane (TMPS) (3.2) Trimethoxy(2-phenylethyl)silane (TMPES)
	(4) Fluorinated	(4.1) Fluorinated ((3,3,3- trifluoropropyl)silane (TMFS) (4.2) 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDES)



Scheme 1. Schematic representation of the procedure for surface modification on glass.



Fig. 1. Contact angle images with water, hexadecane and oleic acid of (a) TEOS-, (b) TMS-, (c) ODS-, (d) ODS/TEOS- and (e) ODS/TMS-glasses.

While TEOS- and ITMS-treated glass surfaces possessed the moderate oleophobicity, TMS-treated surface was rather oleophobic.

The critical surface tension (γ_c) of organosiloxane SAMs [8,17] are listed in Table 2. As the surface tension of n-hexadecane ($\gamma_c = 27.6 \text{ mN/m}$ [4]) is lower than the critical surface tensions ($\gamma_c = 35-42.5 \text{ mN/m}$) of SAMs with hydrophilic moiety, hexadecane spreads easy on the surface of the organosiloxane glass. On the other hand, owing to the higher surface tension of hexadecane than those of TMS- and TMPES-glass surfaces, hexadecane cannot spread on such surfaces. However, this rule was not necessarily applicable to other surfaces.

The substrates with fluorinated moiety exhibited the significantly high contact angles of hexadecane. The amphiphobicity of fluorinated compounds depends on the content of fluorinated groups, since the effects of such factors are derived from the surface tension and influence on subsequent wetting properties [4,18]. The present results clarified that the PFDES-glass surface possessed higher oleophobic property than TMFS-glass due to the existence of several CF₂ groups, which have critical surface tension of 18 mN/m [19]. However, the surface tension (33.5 mN/m) of TMFS-glass from literature [6] was higher than surface tension of hexadecane, although there is a report of critical surface tension of 6–10 mN/m on CF₃-terminated surface [1,2,20]. Then it can be noted that the high oleophobicity (or amphiphobic-ity) of the fluorinated surfaces is caused not only by the polarity of the C–F bond and the weak molecular interaction of fluorinated compounds but also by the close-packing of functional CF₃ terminals [20,21].

It has been proven by examinations using formulated artificial fingerprint liquid that as long as the contact angle with formulated artificial fingerprint is above 87–88°, the surface is anti-fingerprint [22]. Since components of human fingerprint are mainly oleic acid (40.6%) [11], oleic acid can be substitutive for fingerprint. In the present work, oleic acid was regarded as a liquid probe to verify the anti-fingerprint property of the modified glass surfaces because oleic acid is an amphiphilic unsaturated fatty acid with hydropho-

Table 2			
Contact angles with water, n-hexadecane and oleic acid	, and roughnesses of various	s glass surfaces in compariso	n with surface tensions.

Sample	Surface tension (mM/N)	Contact angle			Roughness (nm)
		Water (72.8 mN/m) ³	Hexadecane (27.6 mN/m) ⁴	Oleic acid (31.8 mN/m) ⁵	
Bare glass	47.0 ¹	37 ± 3°	$14 \pm 2^{\circ}$	18 ± 1°	-
<u>Hydrophilic</u>					
APTES-glass	35.0 ¹	80 ± 4°	0°	26 ± 1°	2 ± 0
GPS-glass	42.5 ¹	80 ± 3°	0°	31 ± 4°	5 ± 3
<u>Hydrophobic</u>					
TEOS-glass	23.5 ²	74 ± 4°	15 ± 4°	26 ± 3°	10 ± 6
TMS-glass	22.5 ¹	78 ± 4°	30 ± 6°	41 ± 3°	6 ± 2
ITMS-glass	20.9 ²	92 ± 2°	$18 \pm 4^{\circ}$	35 ± 3°	4 ± 1
ODS-glass	27.6 ²	87 ± 4°	0°	31 ± 4°	2 ± 1
<u>Fluorinated</u>					
TMFS-glass	33.5 ¹	93 ± 5°	$51 \pm 4^{\circ}$	$48 \pm 4^{\circ}$	2 ± 1
PFDES-glass	18.1 ²	93 ± 6°	$69\pm6^{\circ}$	74 ± 1°	12 ± 6
Phenyl					
TMPS-glass	40.0 ¹	90 ± 11°	14 ± 3°	25 ± 6°	13 ± 12
TMPES-glass	28.0 ²	90 ± 2°	$16 \pm 4^{\circ}$	27 ± 4°	12 ± 6
Hvbrid-SAM					
APTES/TMS-glass	_	90 ± 3°	0°	21 ± 1°	2 ± 1
TMFS/TMS-glass	_	92 ± 6°	31 ± 3°	31 ± 4°	2 ± 0
ODS/TEOS-glass	-	68 ± 2°	15 ± 1°	$26 \pm 6^{\circ}$	6 ± 3
ODS/TMS-glass	-	$90 \pm 4^{\circ}$	26 ± 3°	43 ± 3°	8 ± 2

¹ Ref. [10]. ² Ref. [22].

⁵ γ_c = 31.8 mN/m Ref. [22].

bic oleyl moiety and hydrophilic carboxylic acid moiety. The surface tension of oleic acid is 31.8 mN/m [21], which is in the range of those of human fingerprints (20-50 mN/m [22]) and is almost comparative to that of the present organooxysilane-modified glasses (20.9-42.5 mN/m) except PFDES-treated glass. The contact angle of oleic acid was lowest (18°) for bare glass, moderate (25-31°) for substrates with hydrophilic and phenyl moieties, and highest (48° and 74°) for substrates with fluorinated moieties (Fig. 1 and Table 2). Substrates with hydrophobic moieties exhibited various contact angles (26°-41°), depending on the organic moieties. These order tendencies were almost consistent with the tendencies of the oleophobicity from hexadecane contact angles, although the contact angles of oleic acid were larger than those of hexadecane, since the surface tension of oleic acid was higher than hexadecane. As expected, oleic acid contact angle was highest on fluorinated surface. It is especially remarkable that oleic acid contact angle on TMS-glass was only slightly lower than that on TMFS-glass. It should be recalled that the surface tension of TMS is only 22.5 mN/m [20]. Thus, the TMS surface can be considered to be amphiphobic as well as fluorinated surfaces.

The hybrid SAMs with the hydrophilic-hydrophobic moiety (APTES/TMS), hydrophobic-hydrophobic moiety (ODS/TEOS and ODS/TMS) and fluorinated-hydrophobic moiety (TMFS/TMS) were also fabricated on the glass surface by sol-gel method. The results (Fig. 1 and Table 2) revealed the synergistic effect on increase of water contact angle for the hybrids of hydrophobic (TMS) moiety with the hydrophilic (APTES) and hydrophobic (ODS) moieties. That is, the water contact angles were obviously higher on APTES/TMS- and ODS/TMS-glass surfaces (both 90°) than on glass surfaces coated with each component moiety. The water contact angle of TMFS/TMS-glass was almost close to TMFS-glass rather than to TMS-glass, implying the dominant contribution of TMFS. However, hexadecane contact angles seem to be predominated by one of components such as APTES > TMS, TEOS > ODS, TMS > ODS, TMS > TMFS. Concerning oleic acid contact angles, it was noticed that the anti-fingerprint effect of TMFS and TMS decreased after hybridization. Meanwhile, TMS had a superiority in a hybrid with ODS, and the anti-fingerprint effect of hybrid-glass was same as or superior to TMS-glass, although APTES controlled such surface property in the case of APTES/TMS-glass.

The surface concavities may be also one of triggers of the amphiphobic property. The morphologies of glass surfaces were measured on an AFM, as represented in Fig. 2 and Fig. S2. The observed roughness is listed in Table 2. The surfaces of APTES-, ITMS-, ODS- and TMFS-glass surfaces with roughness below 5 nm were smoother than those of other surfaces with roughness up to 30 nm. For the cases of hybrid SAM glass surfaces, the surface morphology was dominated by one of components, that is, by APTES, TMFS, TEOS, and TMS for APTES/TMS-, TMFS/TMS-, ODS/TEOS- and ODS/TMS-glasses, respectively. This phenomenon is consistent with the domination on oleic acid contact angles, as discussed above.

On the other hand, the AFM image of ODS/TMS-glass displayed a lot of protrusions with height below 10 nm on the glass surface (Fig. 2(e)), indicating the fabrication of uniform roughness on the glass surface. The texture of similar rough surface was also visualized even on an AFM image of TMS-glass (Fig. 2(c)), although the rough surface is in domains but not uniform in whole surface. It should be focused that these two SAM glass surfaces presented the high oleic acid contact angles close to TMFS-glass. Therefore, it may be suggested that glass surfaces treated by non-fluorinated TMS organosiloxane and its hybrid with ODS organosiloxane can provide a "bumpy structure" in nm order on the glass and hence enhance the repellency of oleic acid or the amphiphobic character. However, TMFS-glass gives rather smoother surface morphology than TMS-glass and ODS/TMS-glass, although these SAM glasses present a similar amphiphobic property. Moreover, TEOS- and ODS/TEOS-glasses show "bumpy structure" similar to TMS- and ODS/TMS-glasses (Fig. 2) but, nevertheless, the amphiphobic property of the former glasses is different from the latter. These results indicate that the roughness of glass surfaces may not necessarily influence in the anti-fingerprint property.

³ $\gamma_c = 72.8 \text{ mN/m Ref. [4]}.$

 $^{^{4} \}gamma_{c} = 27.6 \text{ mN/m Ref.}$ [6].



Fig. 2. AFM images of (a) TEOS-, (b) ODS-, (c) TMS-, (d) ODS/TEOS-, and (e) ODS/TMS-glass.

4. Conclusions

Organosiloxane with different organic functionality were successfully fabricated on glass surface by using sol-gel technique. The fabrication of organosiloxane on the glass revealed a significant increase in surface hydrophobicity. However, the substrate with methyl terminated (non-fluorinated) organosiloxane (TMS-glass) could provide both amphiphobic and anti-fingerprint properties on surfaces. In addition, the hybrid with both hydrophobic, non-fluorinated moieties (ODS and TMS) could also impart both amphiphobic and anti-fingerprint properties. The surface concavities could be observed on TMS- and ODS/TMS-glass surfaces, indicating that the repellency of oleic acid on surface is also affected by the surface roughness. Then it can be concluded that anti-fingerprint property can be evaluated by contact angle of oleic acid and is related to the amphiphobicity. Both properties are influenced by chemical species at the exposed surface as well as surface roughness and attained even non-fluorinated materials.

Acknowledgements

The authors would like to thank The National Taiwan University of Science and Technology, project number: 100H451201, for the financial support extended to this study. We also give our thanks to Foxlink Co. Ltd., Taiwan, for their financial support. AS gratefully acknowledges the National Taiwan University of Science and Technology, Taiwan, for Postdoctoral Fellowship.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2014.02.066.

References

- H. Meng, S. Wang, J. Xi, Z. Tang, L. Jiang, Facile means of preparing superamphiphobic surfaces on common engineering metals, J. Phys. Chem. C 112 (2008) 11454–11458.
- [2] L. Cao, T.P. Price, M. Weiss, D. Gao, Super water- and oil-repellent surfaces on intrinsically hydrophilic and oleophilic porous silicon films, Langmuir 24 (2008) 1640–1643.
- [3] H. Jin, M. Kettunen, A. Laiho, H. Pynnonen, J. Paltakari, A. Marmur, O. Ikkala, R.H.A. Ras, Superhydrophobic and superoleophobic nanocellulose aerogel membranes as bioinspired cargo carriers on water and oil, Langmuir 27 (2011) 1930–1934.
- [4] H. Bellenger, T. Darmanin, F. Gutittard, Surface structuration (micro and/or nano) governed by the fluorinated tail lengths toward superoleophobic surfaces, Langmuir 28 (2012) 186–192.
- [5] Y. Jung, B. Bhushan, Wetting behavior of water and oil droplets in three-phase interfaces for hydrophobicity/philicity and oleophobicity/philicity, Langmuir 25 (2009) 14165–14173.
- [6] A.G. Kannan, N.R. Choudhury, N. Dutta, Fluoro-silsesquioxane-urethane hybrid for thin film applications, ACS Appl. Mater. Interfaces 1 (2009) 336–347.
- [7] S.M.M. Ramos, A. Benyagoub, B. Canut, C. Jamois, Superoleophobic behavior induced by nanofeatures on oleophilic surfaces, Langmuir 26 (2010) 5141– 5146.
- [8] A. Barry, P. Youlin, Y.M. Kim, The role of polarity in the structure of silanes employed in surface modification, in: K.L. Mittal (Ed.), Silanes and other

coupling agents, 5, Koninklijke Brill NV, Leiden, The Netherlands, 2009, pp. 51–64.

- [9] T. Imae, M. Ito, K. Aoi, K. Tsutsumiuchi, H. Noda, M. Okada, Formation of organized adsorption layer by amphiphilic dendrimers, Colloid Surf. A 175 (2000) 225–234.
- [10] M. Ito, T. Imae, Self-assembled monolayer of carboxyl-terminated poly(amido amine) dendrimers, J. Nanosci. Nanotechol. 6 (2006) 1667–1672.
- [11] Granted Patent: EP 1645681 B1, 2006, Method of providing non-detergent washing function; Components of fingerprint are oleic acid (40.6%), triolein (22.4%), cholesterol olete (17.5%), liquid paraffin (3.6%), squalene (3.6%), cholesterol (2.3%), and gelatin (10.0%).
- [12] D. Onoshima, T. Imae, Dendritic nano- and microhydrogels fabricated by triethoxysilyl focal dendrons, Soft Matter 2 (2006) 141–148.
- [13] K. Mitamura, T. Imae, N. Saito, O. Takai, Fabrication and self-assembly of hydrophobic gold nanorods, J. Phys. Chem. B 111 (2007) 8891–8898.
- [14] A. Vincent, S. Babu, E. Brinley, A. Karakoti, S. Deshpande, S. Seal, Role of catalyst on refractive index tunability of porous silica antireflective coatings by sol-gel technique, J. Phys. Chem. C 111 (2007) 8291–8298.
- [15] J. Choi, I. Lee, S.Y. Lee, Deposition of polypyrrole thin film through the molecular interaction with a designer peptide, Langmuir 25 (2009) 11495– 11502.
- [16] K. Sever, Y. Seki, H. Ali-Gulec, M. Sarikanat, M. Mutlu, I. Tavman, Preparation and characterization of thin film by plasma polymerization of glycidoxypropyltrimethoxysilane at different plasma powers and exposure times., Appl. Surf. Sci. 255 (2009) 8450–8457.
- [17] Royal Society of Chemistry/Advancing the Chemical Sciences, http://www.chemspider.com>.
- [18] R. Campos, A.J. Guenthner, T.S. Haddad, J.M. Mabry, Fluoroalkyl-functinalized silica particles: synthesis, characterization, and wetting characteristics, Langmuir 27 (2011) 10206–10215.
- [19] C. Aulin, S.H. Yun, L. Wagberg, T. Lindstrom, Design of highly oleophobic cellulose surfaces from structured silicon templates, ACS Appl. Mater. Interfaces 1 (2009) 2443–2452.
- [20] N. Ghosh, A. Bajoria, A.A. Vaidya, Surface chemical modification of poly(dimetylsiloxane)-based biomimetic materials: oil-repellent surfaces, ACS Appl. Mater. Interfaces 1 (2009) 2636–2644.
- [21] M. Kobayashi, Y. Terayama, H. Yamaguchi, M. Terada, D. Murakami, K. Ishihara, A. Takahara, Wettability and antifouling behavior on the surfaces of superhydrophilic polymer brushes, Langmuir 28 (2012) 7212–7222.
- [22] L.Y.L. Wu, S.K. Ngian, Z. Chen, D.T.T. Xuan, Quantitative test method for evaluation of anti-fingerprint property of coated surfaces, Appl. Surf. Sci. 257 (2011) 2965–2969.