



Short communication

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

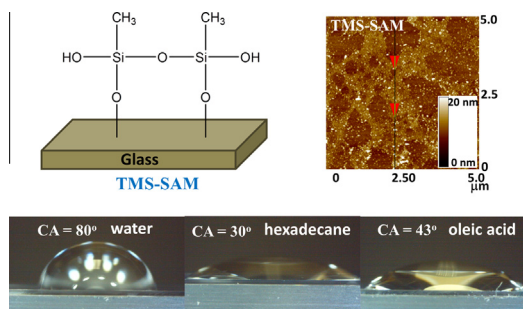
Ampornphan Siriviriyanun ^a, Toyoko Imae ^{a,b,*}^a Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 10607, Taiwan, ROC^b Department of Chemical Engineering, National Taiwan University of Science and Technology, 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.

GRAPHICAL ABSTRACT

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



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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.

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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: imaie@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) of 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 (H_2SO_4 : H_2O_2 = 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

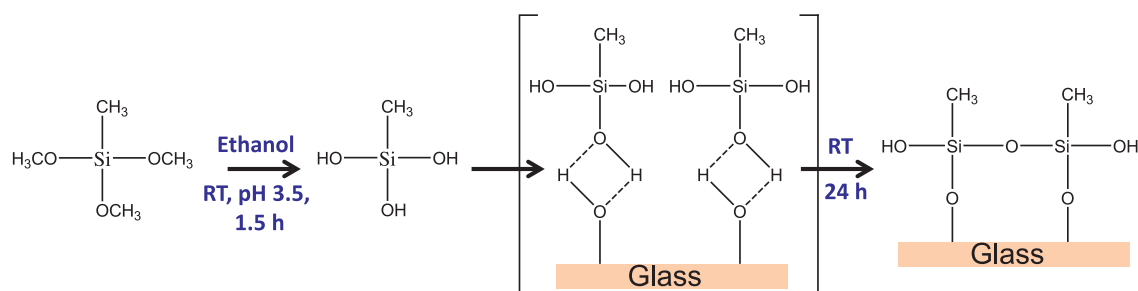
SAMs of organosiloxanes with different organic functions such as hydrophilic, hydrophobic, phenyl and fluorinated moieties as

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 < 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
List of organosiloxanes with different functionalities.

Functionality	Organosiloxane
(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 (trimethoxyphenyl)silane (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.

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