



# Self-assembled perfluoroalkylsilane films on silicon substrates for hydrophobic coatings



Lu Cai<sup>a,b</sup>, Anqi Liu<sup>a</sup>, Yanhua Yuan<sup>a</sup>, Li Dai<sup>a</sup>, Zhanxiong Li<sup>a,c,\*</sup>

<sup>a</sup> College of Textile and Clothing Engineering, Soochow University, Suzhou 215021, China

<sup>b</sup> College of Textile and Clothing, Yancheng Institute of Technology, Yancheng 224051, China

<sup>c</sup> National Engineering Laboratory for Modern Silk, Suzhou 215123, China

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## ABSTRACT

In this work, four novel perfluoroalkylsilanes were included to fabricate hydrophobic coatings on silicon substrates by the method of self-assembled films. The surface chemical compositions and structures of self-assembled perfluoroalkylsilane films were analyzed by X-ray photoelectron spectroscopy and energy dispersive X-ray spectrometer, and results showed that perfluoroalkylsilane molecules have uniformly assembled onto the surface of hydroxylated silicon substrate successfully. Water contact angles and surface free energy were tested to characterize the surface wettability of self-assembled perfluoroalkylsilane films. Results showed that the self-assembled bisfluorooctyltrichlorosilane film with annealing process (BPFOTS-Si-heat) had the highest water contact angle as  $117.6 \pm 0.9^\circ$  and hexadecane contact angle as  $76.7 \pm 1.3^\circ$ . This may be attributed to the incorporation of two longer perfluoroalkyl groups into the silane molecule. On the other hand, annealing process also contributed much to improve the hydrophobicity of self-assembled films. The adhesive force of annealed self-assembled perfluoroalkylsilane films was lower than that of untreated ones. Dynamic contact angle measurement showed that the BPFOTS-Si-heat had the smallest water contact angle hysteresis ( $14 \pm 2^\circ$ ) and hexadecane contact angle hysteresis ( $10 \pm 2^\circ$ ). Surface morphology of self-assembled films with different assembling time was obtained through atomic force microscopy, and the surface was found to be gradually covered by dense sharp peaks with the extension of assembling time.

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## 1. Introduction

A surface with water contact angle larger than  $90^\circ$  is usually called a hydrophobic surface, which has attracted a great deal of attention [1]. Generally speaking, a hydrophobic surface can be fabricated by two different ways: (a) increasing the surface roughness of hydrophobic substrates, (b) physically spinning coating films or chemically assembling materials with low surface free energy onto the surface of substrates [2–5]. Among different approaches, self-assembled films, including self-assembled monolayers, have been found to be an excellent method to create hydrophobic coatings [6,7], which exhibit great advantages of simple preparation method, high orderliness and orientation, less defects, tunability of physical and chemical properties and exceptional stability [8–10]. Except the hydrophobic coatings, self-assembled films also have

been extensively used in the fields of lubricant films [11–13], electrochemistry [14,15], biological application [16], drug delivery [17] and other functional surfaces due to their excellent performance.

Usually, two approaches, including vapor phase deposition and liquid phase deposition, have been mainly adopted to prepare the self-assembled films. The vapor phase deposition can provide good control of the reagent supply and avoid problems such as diffusion transport of reagents into substrate, solution concentration and solvent waste [18,19]. While the liquid phase deposition is easier to be achieved and widely adopted by many researchers, so great efforts have been put into studying and optimizing the factors that affect the film formation. It has been reported that the formation of self-assembled films by liquid phase deposition depends significantly on various parameters such as type of solvents [20,21], precursor concentration [22,23], moisture content of the solvent or substrate surface [22,24], assembling time [25,26] and reaction temperature [24], etc.

Self-assembled films are obtained by spontaneously chemical absorption of molecules to form a thin coating on a substrate [27]. In the formation of self-assembled films, organosilanes have

\* Corresponding author at: College of Textile and Clothing Engineering, Soochow University, No. 199 Renai Road, Industry Park, Suzhou 215021, China.

E-mail address: [lizhanxiong@suda.edu.cn](mailto:lizhanxiong@suda.edu.cn) (Z. Li).

attracted researchers' widespread interests. Due to their excellent bonding strength, low surface free energy and good thermal stability, they are usually considered as promising candidates for hydrophobic coatings [7,8,18,28,29]. The functional organosilanes have  $X_n\text{-Si}(\text{R-Y})_{4-n}$  as general structure, in which X represents a hydrolysable group that chemisorbs to the substrate, mostly alkoxy or chlorine; R is the spacer or linker group; Y means the organofunctional group that determines the interfacial properties of self-assembled films [30–33]. Generally, the formation mechanism of the organosilane-based self-assembled films using the method of liquid phase deposition can be explained by following procedures: Firstly, the hydrolysable groups of organosilanes are hydrolyzed by the trace amount of water molecules that exist in the solvent to form active silanol groups (Si-OH). Second, the hydrolysed organosilanes adsorb on the surface of hydroxyl terminated substrates through hydrogen bonding. Next, condensation takes place where silanol groups further covalently link with each other and with the hydroxyl groups on the substrate surface, forming a siloxane network (Si-O-Si) and metal-siloxane (Si-O-Metal) bonds [6,12,34]. Finally, the organosilanes are aggregated, which are driven by attractive forces such as van der Waals forces, dipole-dipole interactions or hydrogen bonding between the hydrocarbon chains to obtain stable, ordered and densely packed self-assembled films [14,32,35–38]. Therefore, the stability of organosilane-based self-assembled films on metal oxides is obviously determined by one or more of the following chemical bonds: (a) covalent bonds between silane molecules and the substrates; (b) cross-links between neighboring silane molecules; (c) hydrogen bonds between the silanol groups of silane molecules; (d) van der Waals interactions between alkyl chains [39].

Among various organosilanes, perfluoroalkylsilanes are the most extensively used surface modification agents for generating self-assembled films on a variety of substrates such as steel, titanium, silicon, copper and aluminum [6–8,10,39,40–43]. Based on the excellent properties of C-F bonds, perfluoroalkylsilanes present good thermal and chemical stability, liquid repellency, low surface free energy and coefficient of friction [6,13,36,44,45], etc, which make them widely used in hydrophobic coatings.

In this paper, we investigated four different perfluoroalkylsilanes as shown in Fig. 1, which included  $\gamma$ -{4-mono(1H,1H,2H,2H-nonafluorohexylmethoxyl)-[1,2,3]-triazolo}propyl-trichloro-silane (MPFHSTs),  $\gamma$ -{4-mono(1H,1H,2H,2H-tridecafluorooctylmethoxyl)-[1,2,3]-triazolo}propyl-trichloro-silane (MPFOTS),  $\gamma$ -{4-bis(1H,1H,2H,2H-nonafluorohexyl)succinate-[1,2,3]-triazolo}propyl-trichloro-silane (BPFHSTs) and  $\gamma$ -{4-bis(1H,1H,2H,2H-tridecafluorooctyl)succinate-[1,2,3]-triazolo}propyl-trichloro-silane (BPFOTS). These perfluoroalkylsilanes were self-assembled onto the silicon substrates by the method of liquid phase deposition, then self-assembled films with different assembling time were studied and characterized by X-ray photoelectron spectroscopy, energy disperse X-ray spectroscopy, contact angle and surface free energy, adhesive force measurement and atomic force microscopy.

## 2. Experimental

### 2.1. Materials

Acetone and ethanol were purchased from Qiangsheng Functional Chemicals Co., Ltd. and were used as supplied. Tetrahydrofuran (THF) was purified by distillation with benzophenone as indicator, which was obtained from Shanghai SQS Chemical Co., Ltd. 1H,1H,2H,2H-tridecafluorooctyl-trichloro-silane (FOTS) was obtained from Hengtong Fluorine Chemical technology Co., Ltd.

Trichlorosilane was supplied by Chenguang Chemicals Co., Ltd. Karsedt's catalyst was supplied by Sigma-aldrich Life Science & Technology Co., Ltd. One-side polished n-type silicon wafers (one hundred oriented, with resistivity of 0.01–0.09  $\Omega/\text{cm}$  and thickness of  $400 \pm 20 \mu\text{m}$ ) were purchased from Xinxing Braim Technology Co., Ltd.

### 2.2. Synthesis of perfluoroalkylsilanes

Synthetic routes to the four different perfluoroalkylsilanes are shown in Fig. 1, in which the 1-allyl-4-mono(1H,1H,2H,2H-perfluoroalkyl)methoxyl-[1,2,3]-triazole and 1-allyl-4-bis(1H,1H,2H,2H-perfluoroalkyl)succinate-[1,2,3]-triazole were prepared according to our previous reported literature [46].

#### 2.2.1. $\gamma$ -{4-mono(1H,1H,2H,2H-nonafluorohexylmethoxyl)-[1,2,3]-triazolo}propyl-trichloro-silane (MPFHSTs)

The synthetic procedure of MPFHSTs in Fig. 1(A) was carried out as follows: to a 50 mL three-necked round flask equipped with condenser and thermometer, 0.02 mol 1-allyl-4-mono(1H,1H,2H,2H-perfluorohexyl)methoxyl-[1,2,3]-triazole and 10 mL toluene were added and stirred for 10 min at 70 °C under the nitrogen atmosphere, followed by the addition of one drop of Karstedt's catalyst. Then 0.02 mol trichlorosilane was added, and the reaction mixture was stirred constantly at 70 °C for 4 h. After the reaction was completed, the solvent was removed under reduced pressure to give the MPFHSTs.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (s, 1H,  $\text{C}_{\text{triazole-H}}$ ), 4.82 (s, 2H,  $\text{C}_{\text{triazole-CH}_2}$ ), 4.02 (t, 2H,  $J=6.2$  Hz,  $\text{N}_{\text{triazole-CH}_2}$ ), 3.91 (t, 2H,  $J=6.6$  Hz,  $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2$ ), 2.43 (dt, 2H,  $J=18.6, 6.5$  Hz,  $\text{C}_4\text{F}_9\text{CH}_2$ ), 1.80 (m, 2H,  $\text{SiCH}_2$ ), 1.05 (m, 2H,  $\text{SiCH}_2$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.7 ( $\text{C}_{\text{triazole-CH}_2\text{O}}$ ), 122.3 ( $\text{C}_{\text{triazole-H}}$ ), 64.5 ( $\text{C}_{\text{triazole-CH}_2\text{O}}$ ), 62.6 ( $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{O}$ ), 52.8 ( $\text{N}_{\text{triazole-CH}_2}$ ), 31.6 ( $\text{C}_4\text{F}_9\text{CH}_2$ ), 24.5 ( $\text{SiCH}_2\text{CH}_2$ ), 14.1 ( $\text{SiCH}_2$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -81.1 (3F,  $\text{CF}_3$ ), -113.8 (2F,  $\text{CF}_3\text{CF}_2$ ), -124.0 (2F,  $\text{CF}_3\text{CF}_2\text{CF}_2$ ), -126.6 (2F,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2$ ); FT-IR (KBr): 3139.0, 3093.1, 2970.9, 1239.8, 1210.6, 1134.4  $\text{cm}^{-1}$ .

#### 2.2.2. $\gamma$ -{4-mono(1H,1H,2H,2H-tridecafluorooctylmethoxyl)-[1,2,3]-triazolo}propyl-trichloro-silane (MPFOTS)

The synthetic procedure of MPFOTS in Fig. 1(B) was similar to the synthetic procedure of MPFHSTs.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (s, 1H,  $\text{C}_{\text{triazole-H}}$ ), 4.86 (s, 2H,  $\text{C}_{\text{triazole-CH}_2}$ ), 4.05 (t, 2H,  $J=6.2$  Hz,  $\text{N}_{\text{triazole-CH}_2}$ ), 3.86 (t, 2H,  $J=6.6$  Hz,  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$ ), 2.41 (dt, 2H,  $J=18.8, 6.5$  Hz,  $\text{C}_6\text{F}_{13}\text{CH}_2$ ), 1.78 (m, 2H,  $\text{SiCH}_2\text{CH}_2$ ), 1.09 (m, 2H,  $\text{SiCH}_2$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.6 ( $\text{C}_{\text{triazole-CH}_2\text{O}}$ ), 122.3 ( $\text{C}_{\text{triazole-H}}$ ), 64.8 ( $\text{C}_{\text{triazole-CH}_2\text{O}}$ ), 62.6 ( $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{O}$ ), 52.8 ( $\text{N}_{\text{triazole-CH}_2}$ ), 31.5 ( $\text{C}_6\text{F}_{13}\text{CH}_2$ ), 24.9 ( $\text{SiCH}_2\text{CH}_2$ ), 14.3 ( $\text{SiCH}_2$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -81.1 (3F,  $\text{CF}_3$ ), -116.8 (2F,  $\text{CF}_3\text{CF}_2$ ), -122.3 (2F,  $\text{CF}_3\text{CF}_2\text{CF}_2$ ), -123.0 (2F,  $\text{CF}_3(\text{CF}_2)_2\text{CF}_2$ ), -123.5 (2F,  $\text{CF}_3(\text{CF}_2)_3\text{CF}_2$ ), -126.5 (2F,  $\text{CF}_3(\text{CF}_2)_4\text{CF}_2$ ); FT-IR (KBr): 3138.6, 3093.7, 2918.7, 1240.6, 1211.6, 1151.1, 1099.4  $\text{cm}^{-1}$ .

#### 2.2.3. $\gamma$ -{4-bis(1H,1H,2H,2H-nonafluorohexyl)succinate-[1,2,3]-triazolo}propyl-trichloro-silane (BPFHSTs)

The synthetic procedure of BPFHSTs in Fig. 1(C) was similar to the synthetic procedure of MPFHSTs.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (s, 1H,  $\text{C}_{\text{triazole-H}}$ ), 4.30 (m, 4H,  $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2$ ), 4.06 (m, 2H,  $\text{N}_{\text{triazole-CH}_2}$ ), 3.96 (m, 1H,  $\text{CH}_2\text{OOCCH}$ ), 3.82 (m, 2H,  $\text{C}_{\text{triazole-CH}_2}$ ), 3.02 (m, 2H,  $\text{CH}_2\text{OOCCH}_2$ ), 2.56 (m, 4H,  $\text{C}_4\text{F}_9\text{CH}_2$ ), 1.75 (m, 2H,  $\text{SiCH}_2\text{CH}_2$ ), 0.88 (m, 2H,  $\text{SiCH}_2$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.7 ( $\text{CH}_2\text{OOCCH}$ ), 169.9 ( $\text{CH}_2\text{OOCCH}_2$ ), 144.3 ( $\text{C}_{\text{triazole-CH}_2}$ ), 121.9 ( $\text{C}_{\text{triazole-H}}$ ), 60.2 ( $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2$ ), 52.9 ( $\text{N}_{\text{triazole-CH}_2}$ ), 41.3

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