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Preparation of highly hydrophobic and oleophobic textile surfaces using microwave-promoted silane coupling

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Abstract The wetting behavior of a solid surface is controlled by the geometric structure as well as the chemical composition of the material. In this study, highly hydrophobic and oleophobic materials were prepared by microwave-assisted cross-linking of perfluoroalkoxysilane onto nylon and cotton-blended fabric. Surface roughness was controlled by choice of the catalyst. Water catalysis resulted in a smooth coating deposition of the perfluoroalkoxysilanes on the fiber surface, while base catalysis resulted in a micro and nano scale rough surface on the fibers. Both water and base-catalyzed materials were superhydrophobic, but creating multi-scale geometric structure via base catalysis was required to improve oleophobicity. A series of experiments explored the parameters of fluorosilane concentration, base catalysis, curing time, and the number of cures. The apparent contact angles of the fabric samples treated in a multiple dip-and-cure sequence averaged 135° (hexadecane) and 148° (water) with no absorption of either within 60 h (hexadecane) or until complete evaporation (water).

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Introduction

The wetting behavior of soft materials has gained a great deal of interest and has been studied extensively [1–5]. Our interests extend beyond bio-mimicry of the much studied, superhydrophobic lotus leaf to achieve similar repellency to oils—a feat not currently found in nature [6–8]. One of the most-prized features of superhydrophobic, low roll-off angle materials are their ability to self-clean—that is the ability of water to collect and remove dirt and debris as the water droplet rolls off the surface of the material [9–11]. Several methods for forming such materials with textiles have been developed in both academia and industry. These methods typically involve drying and curing, e.g., 80–200 °C for 10–60 min, which results in major energy consumption during the finishing process [12]. The use of microwaves for chemically modifying textile surfaces could provide significant advantages over conventional systems with regard to reducing the time and energy needs associated with conventional textile finishing [13].

Just as a surface having a contact angle of <90° to a liquid is considered *philic* for that liquid, e.g., hydrophilic, a surface having a contact angle exceeding 90° to a liquid is defined as *phobic* for that liquid, e.g., hydrophobic [14]. A highly hydrophobic and oleophobic surface can be achieved by satisfying two conditions: a properly designed surface morphology and a low surface energy [6]. A properly roughened surface can be designed with the Cassie–Baxter model. In the Cassie–Baxter model, a liquid sits atop a composite surface, wherein the droplet is in contact with both the material surface, and a gas, typically air. In this approach, a contact angle at a rough surface can be described as [15]:

$$\cos\theta_r^{\mathrm{CB}} = f_1 \cos\theta_e - f_2 \qquad (1)$$

where θ_r^{CB} is an apparent contact angle on a Cassie–Baxter surface; f_1 is the proportion of a wet solid area, i.e., the surface area of the liquid in contact with solid divided by the projected area; f_2 is the proportion of air, the surface area of the liquid in contact with air divided by the projected area; and θ_e is the Young contact angle on the corresponding flat surface. The relation between the surface tension and the Young contact angle is obtained by the Young equation as [16]:

$$\cos \theta_e = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad (2)$$

where γ is the surface tension; and S, SL, and L are the solid–vapor, the solid–liquid, and the liquid–vapor interfaces, respectively. According to the Young equation, the contact angle is a well-defined property that depends on the surface tension coefficients of solid, liquid, and gas. According to Eqs. 1 and 2, reducing γ_S is required to increase high θ_e, and high θ_e and f_2 are essential to obtain θ_r^{CB}. In this study, we decrease γ_S in Eq. 2 by attaching fluorosilane on a 50:50 nylon:cotton blended woven fabric (NyCo, θ_r^{CB} of water and oil $\sim 0°$) via microwave synthesis, and increase f_2 in Eq. 1 using woven fabric structures.

Experimental

Materials

Nylon/cotton 50:50 blended woven fabric (NyCo, Bradford Dyeing Associates) was used as a rough surface after washing with isopropyl alcohol (C_3H_8O, Fisher) before surface modification. Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (FS, $C_{13}H_{13}F_{17}O_3Si$, Gelest), tetramethylorthosilicate (TMOS, $C_4H_{12}O_4Si$, Aldrich), tetraethylorthosilicate (TEOS, $C_8H_{20}O_4Si$, Aldrich), 3-aminopropyltriethoxysilane (APTS, $C_6H_{23}O_3NSi$, Aldrich), ammonium hydroxide (NH_4OH, Mallinckrodt Chemical), and methanol (CH_3OH, Aldrich) were used without further purification. Distilled water and hexadecane ($C_{16}H_{34}$, Aldrich) were used as liquids to measure contact angles.

Grafting of fluorosilane

Experimentation began by replicating the silane grafting process developed by Hoefnagels et al. and Stoeber et al. [17, 18] except that the technique was modified to use microwave radiation. A treatment cycle consists of a three-dip-three-cure process (3D3C)—a swatch of NyCo fabric is saturated in a solution containing FS, squeezed at 100% wet pick-up to remove excess liquid, and cured in a conventional microwave oven at 1250 W(NN-SD967S, Panasonic), with irradiation times varying time from 0 to 60 s. This di-and-cure process is performed thrice, after which the treated samples are rinsed thoroughly with isopropyl alcohol at 20 °C and dried overnight at room temperature.

Characterization

The rough surface of the treated NyCo fabric was examined with a scanning electron microscope (SEM, Hitachi S-3200N) operated at 5 and 10 kV and magnifications from ×25 to ×10,000. Revolution^{TM} v1.60b24 (4pi Analysis Inc) was used for analysis of SEM images. The atomic composition at the surface of treated and untreated fabrics was obtained using X-ray photoelectron spectroscopy (XPS, Kratos Analytical Axis Ultra).

Contact angle measurement

The contact angles of 10 μL water and hexadecane sessile drops were measured on the prepared surfaces using a goniometer (DSA 100, Kruss) at 20 °C. The range of contact angles was obtained from at least five individual measurements, each on a new spot. In addition, the average of five measurements of time-to-absorption, the time until the droplets were fully absorbed into the fabric, was recorded for each liquid droplet on each fabric over a 20-min interval.

Results and discussion

Again, a combination of surface roughness and low surface energy is required to prepare highly hydrophobic and oleophobic materials. While the surface energy of NyCo decreases by FS grafting, silane can form micro- and nano-scale roughness on NyCo and create a high surface area if the FS imparts particulate condensation to the NyCo. Using perfluoroalkoxysilanes in conjunction with corrugated, rough surfaces, FS can build multi-scale roughness having low surface energy. Indeed, the previous research presented that the use of condensed silanes increased micro and nano structure corrugation and resulted in the hydrophobicity and oleophobicity of cotton [17]. A highly hydrophobic and oleophobic NyCo rough surface can be developed in the same manner by covalently binding silanes onto the NyCo surface. Such treatment methods correlate easily to a wide variety of textiles that have –OH and –NH groups such as cotton, polyamides, polyaramids, etc. Fluoroalkyl chains can be attached to the –OH or –NH site via a siloxane or silazane linkage as shown in Fig. 1.

Use of microwave radiation in this process greatly enhances the reaction rate of the covalent attachment of

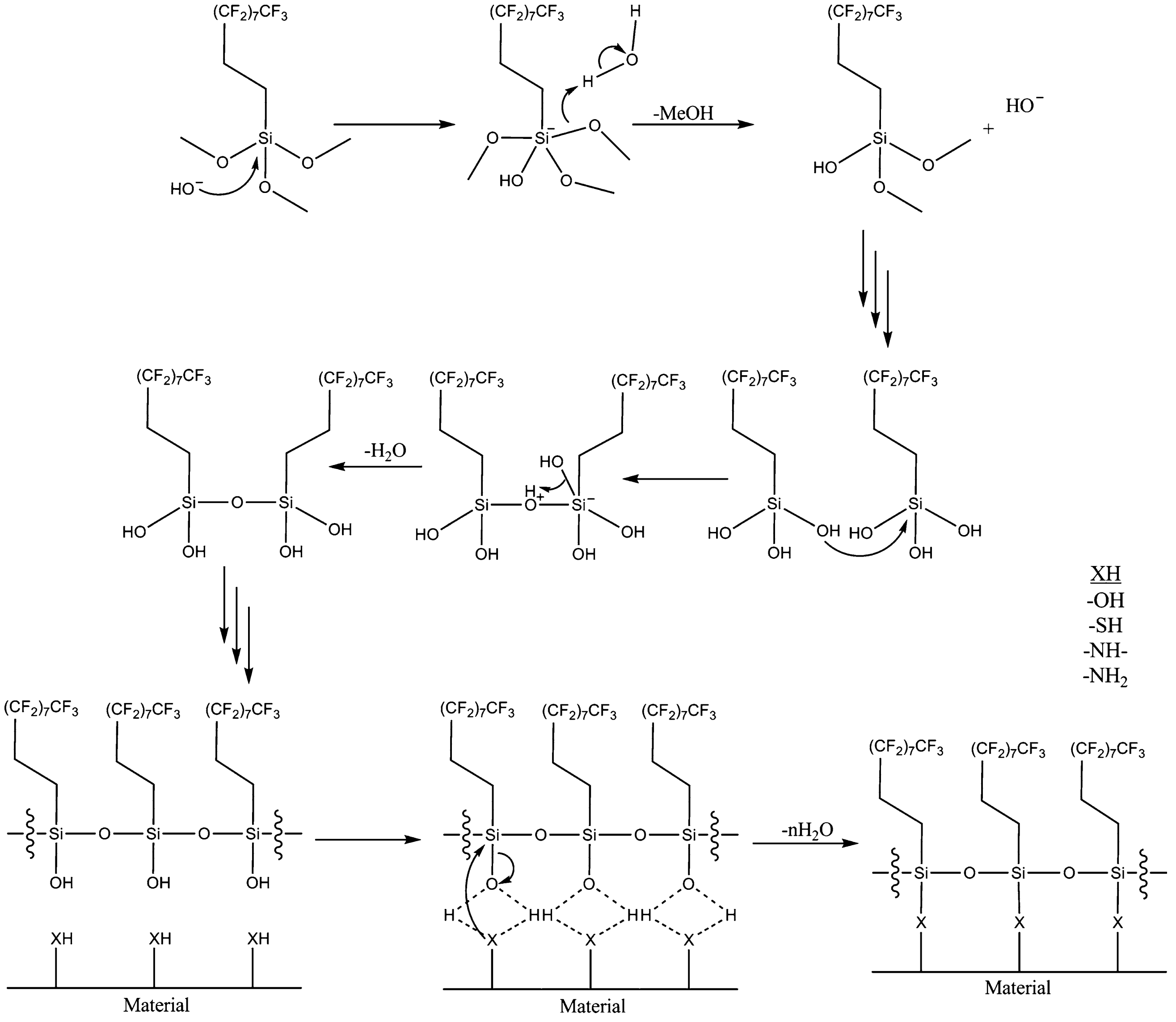


Fig. 1 Reaction of a substrate containing alcohol, amine, or thiol functional groups with a perfluoroalkyltrimethoxysilane in alkaline solution. (Source: Lee and Owens [6])

silanes to the reactive substrates, as does the presence of acid or base. Since treatment at low pH is avoided for the treatment of cotton and other cellulose derivatives due to the instability of the β-acetal bonds in acidic solutions, this reaction was processed using neutral and basic solutions. Although any soluble base can be an efficient catalyst, we use ammonium hydroxide as a base catalyst to accelerate the displacement of the methoxy or ethoxy substituent, and to facilitate the formation of the corrugated nano- and micro-structure. Base-catalyzed covalent attachment of colloidal particles that form in FS solution provides micro- and nano-scale roughness to NyCo, while the NyCo fibers treated with a FS solution and water provide little to no particulate condensation as shown in Fig. 2.

Since FS-treated NyCo without catalytic base has a relatively smooth surface while NyCo treated with FS in the presence of 1% catalytic base has multi-scale roughness on the surface, the XPS of both FS-treated NyCo with and without base catalyst was measured and compared with the XPS of untreated NyCo. Figure 3 shows the peaks of C, N, O, F, and Si of (a) NyCo treated in a 10% solution of FS with catalytic water, (b) NyCo treated in a 10% solution of FS in the presence of 1% NH_4OH, and (c) untreated NyCo. Based on the atomic composition in Fig. 3, the ratio of F/O, F/C, C/O, and F/Si at the surface of all three materials were obtained. Table 1 shows that both (a) and (b) have the same amount of fluorine regardless of the presence of base catalyst. However, as shown in Fig. 2, (a) exhibits very

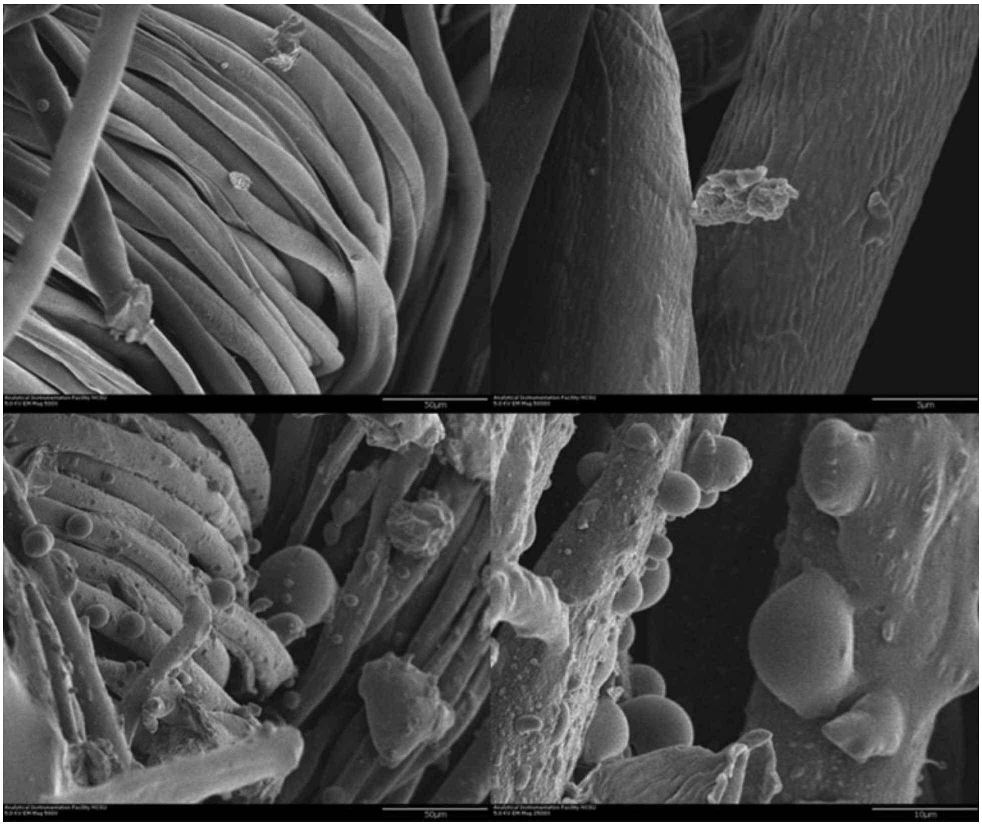


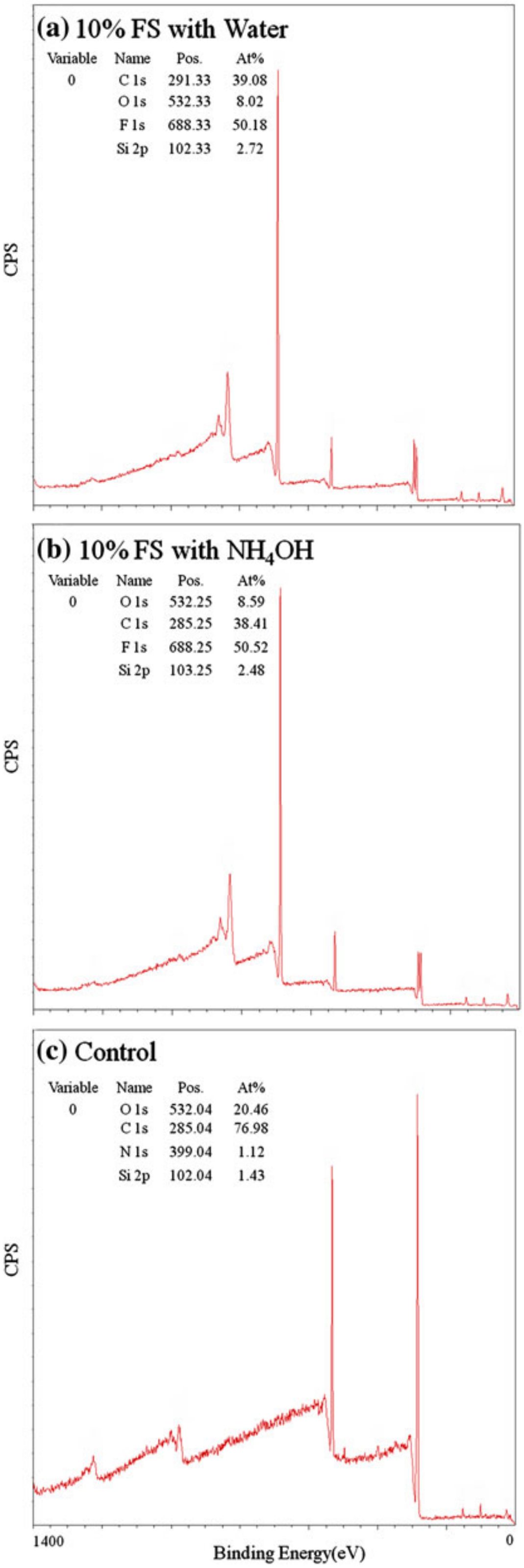
Fig. 2 Microstructure of treated NyCo. NyCo fibers treated in a 10% solution of FS with catalytic water (*above*) and NyCo fibers treated in 10% FS with NH_4OH (*below*)

different surface morphology compared to (b) although they possess almost the same atomic composition of fluorine at the binding energy of 688.3 eV and nearly the same values of F/O, F/C, C/O, and F/Si ratios at the surface. On the other hand, based on the atomic composition of (c), the untreated NyCo does not have fluorine on the surface.

In addition, the role of the pretreatment was determined by treating NyCo with other siloxanes. The presence of additional siloxanes, such as residues of TMOS or TEOS and ATS, before NyCo is treated with FS provide no benefit to the hydrophobicity or oleophobicity of NyCo. Indeed, previous research noted that the use of siloxanes in conjunction with fluorochemicals can reduce the oil repellency [19]. Here, the low surface energy material described is a FS. Using TMOS or TEOS as a pretreatment to condense particles without the use of a base and subsequently coating the NyCo fabric with FS does create a hydrophobic and oleophobic surface; however, such pretreatment provides no discernable advantage over a single base-catalyzed treatment with FS other than the ease of condensing siloxane particles from TMOS or TEOS using microwaves.

Particulate condensates were observed to form on NyCo fabric prepared from irradiated TMOS or TEOS regardless of the presence or absence of base; however, the attachment of condensates in solutions of FS occurred only in the presence of NH_4OH. This suggests that the microwave curing regimen alone is sufficient to initiate the precipitation process within the TMOS and TEOS-treated NyCo, but not the FS-treated NyCo. It is surmised that the alkyl group on FS serves to stabilize the siloxane from methoxy or ethoxy displacement through a combination of steric hindrance and lower Lewis acidity of the silicon center. These two effects make the silicon in a perfluorotrialkoxysilane much less prone to nucleophilic attack than its tetraalkoxysilane counterpart.

The liquid repellency of NyCo treated with FS in a 3D3C process was evaluated by measuring apparent contact angles of water and hexadecane on NyCo. This dip-and-cure process was performed thrice, for a total of three 30 s microwave irradiation intervals. Table 2 presents the contact angles on NyCo when the concentration of FS was varied from 0 to 15% in NH_4OH consisting of isopropyl alcohol. Note that NyCo having 0% FS was treated with TMOS, illustrating the profound effect of the FS substituent on oleophobicity. It is clear that over 1% FS in the solution does not offer significant advantage in either hydrophobicity or oleophobicity.



Variable	Name	Pos.	At%
0	C 1s	291.33	39.08
	O 1s	532.33	8.02
	F 1s	688.33	50.18
	Si 2p	102.33	2.72

Variable	Name	Pos.	At%
0	O 1s	532.25	8.59
	C 1s	285.25	38.41
	F 1s	688.25	50.52
	Si 2p	103.25	2.48

Variable	Name	Pos.	At%
0	O 1s	532.04	20.46
	C 1s	285.04	76.98
	N 1s	399.04	1.12
	Si 2p	102.04	1.43

Fig. 3 XPS of NyCo treated in a 10% solution of FS with catalytic water (**a**), NyCo treated in 10% FS with NH$_4$OH (**b**), and untreated NyCo (**c**)

To extend investigation into the effect of a base catalyst and determine the most efficient length of curing time, a series of NyCo swatches were treated with FS as described above with and without NH$_4$OH. Table 3 demonstrates that the treatment renders NyCo hydrophobic and oleophobic when treated with 1% FS solution in the presence of base catalysis, while NyCo becomes hydrophobic but remains oleophilic when the reaction is catalyzed with water. As shown in Fig. 2, NH$_4$OH can assist in particulate condensation of FS, provides a higher degree of roughness to the FS-treated NyCo than water, and consequently, creates more f_2 in Eq. 1, thus leading to increases in θ_r^{CB} (the apparent contact angle) as presented in Table 3. Figure 4 presents a schematic image of a water droplet sitting on top of the surface of a NyCo fiber treated with FS in the presence of base catalyst; base-catalyzed covalent attachment of colloidal particles that form in FS solution provides multi-scale roughness as well as low surface energy to the NyCo fibers. Based on Fig. 4, Eq. 1 can be modified to:

$$\cos\theta_r^{\mathrm{CB}} = \frac{2R(\pi-\theta_e)}{D}\cos\theta_e + \frac{2R\sin\theta_e}{D} - 1 \qquad (3)$$

where R is the radius of a protuberance that directly contacts water, and D is the center-to-center distance between two protuberances. This equation can provide the apparent contact angles on fibers, yarns, and fabrics. As a numerical example, if $\theta_e \sim 95°$, $R \sim 5$ μm, and $D \sim 15$ μm, θ_r^{CB} on a fiber surface is 115°. In the same manner, if the edge-to-edge distance ($D - 2R$) between two fibers are the same with the diameter ($2R$) of fibers and $D - 2R$ between two yarns are the same with $2R$ of yarns, θ_r^{CB} on a multi-filament yarn will be 142° and a fabric made of this yarn will become superhydrophobic (>150°). However, with the same parameters, a FS-treated NyCo fabric having no protuberances on the fiber surface will have lower contact angles to liquids, and the fabric can be hydrophobic but oleophilic.

In addition, according to the contact angle data presented in Table 3, 10–15 s curing is sufficient to treat NyCo with FS in the presence of NH$_4$OH under microwave synthesis. The apparent contact angles of water and hexadecane on such hydrophobic oleophobic surfaces do not change over several hours or until water evaporates after microwave-associated FS treatment, while untreated NyCo absorbs both water and hexadecane instantly.

The number of cures changes the wetting behavior of FS-treated NyCo when the samples are treated without base catalysis. However, neither hydrophobicity nor oleophobicity of NyCo treated with FS in the presence of NH$_4$OH is affected by the number of cures (Table 4).

Table 1 XPS atomic composition of FS-treated and untreated NyCo

Fabric	Atomic composition (%)				Ratio			
	O	C	F	Si	F/O	F/C	C/O	F/Si
FS-treated NyCo with water	8.0	39.1	50.2	2.7	6.3	1.3	4.9	18.4
FS-treated NyCo with NH_4OH	8.6	38.4	50.5	2.5	5.9	1.3	4.5	20.4
Control NyCo	20.5	77.0	0.0	1.4	0.0	0.0	3.8	0.0

Table 2 Contact angles of water and oil on FS-treated NyCo in the presence of 1% catalytic NH_4OH in isopropyl alcohol

FS (%)	Contact angles (°)	
	Water	Hexadecane
0[a]	142–149	0
1	146–150	120–131
5	150–151	125–131
10	142–146	106–131
15	146–150	113–136

[a] Treated in a solution of 10% TMOS with 1% NH_4OH

Table 3 Effect of curing time and catalyst on the contact angles of water and oil on FS-treated NyCo fabric

Curing time (s)	Contact angles (°)			
	Water catalysis		NH_4OH catalysis	
	Water	Hexadecane	Water	Hexadecane
0	145–151	0	142–152	0
5	140–156	0	143–161	123–136
10	150–151	0	145–149	129–141
15	147–157	0	145–151	135–137
30	136–160	0	143–155	130–139
45	144–162	0	142–153	126–136
60	145–154	0	143–157	131–133

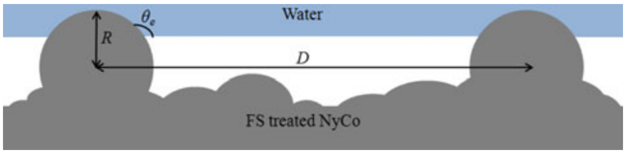


Fig. 4 A water drop on top of a NyCo fiber treated in a 10% FS solution consisting of base catalyst

A NyCo sample treated with 1% FS in isopropyl alcohol—containing also NH_4OH under a 30 s microwave irradiation interval averages an apparent contact angle of 147° with water and 135° with hexadecane regardless of the number of cures (Fig. 5). NyCo fabric treated in this manner is nearly superhydrophobic ($\theta_r^{CB} = 150°$) until complete evaporation of the water droplet and prevented the absorption of hexadecane for over 60 h with almost no change of contact angle. However, water-catalyzed NyCo tends to absorb hexadecane over time, although it takes a longer time for hexadecane to be drawn into the fabric structures of NyCo when the number of cures increases, e.g., the absorption time was improved from 0 to 10 min when the number of curing was varied from 1 to 5 times.

Table 4 Apparent contact angles of water and oil on NyCo fabric samples treated with FS for 30 s via microwave treatments (1–5 times)

Number of cures	Contact angles (°)			
	Water catalyst		NH_4OH catalyst	
	Water	Hexadecane	Water	Hexadecane
1	139–156	0	142–161	126–141
2	142–158	0	143–154	133–152
3	144–159	129[a]	142–158	130–156
4	142–160	126[a]	146–155	131–141
5	155–157	130[a]	146–152	130–140

[a] Initial contact angles. The droplets were absorbed immediately

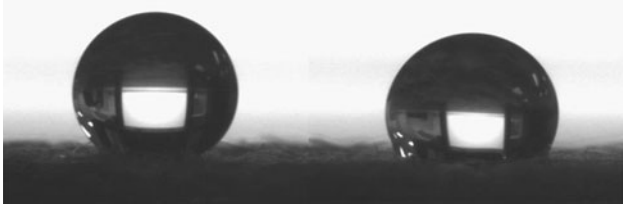


Fig. 5 10 μL water (*left*) and hexadecane (*right*) droplets sitting on top of NyCo treated with FS via microwave synthesis

Interestingly, the water contact angles of all FS-treated samples are very similar. The FS concentration, curing time, and the number of cures affect the oleophobicity of FS-treated NyCo but do not significantly change the hydrophobicity of the treated fabric. This indicates that water contact angles cannot be greatly improved by only varying the parameters discussed in this research. We suggest that improving the macro-scale geometric morphology of NyCo, such as controlling the fiber spacing and manipulating the fabric structure, is also necessary to design and prepare superhydrophobic and superoleophobic surfaces.

Conclusions

A base-catalyzed method for the synthesis of hydrophobic and oleophobic NyCo has been established that requires as little as 1% of FS and can be cured via microwaves. Base catalysis was determined to be critical for synthesizing fabric that would repel hexadecane, e.g., NyCo treated with FS and NH_4OH were significantly more hydrophobic and oleophobic than that treated with FS without NH_4OH. Initial contact angles for base-catalyzed and uncatalyzed NyCo were similar; however, uncatalyzed NyCo tended to absorb the liquids over time, while NyCo treated with NH_4OH repelled water droplets until the droplets completely evaporated and repelled hexadecane for extended periods of time. This indicates that the multi-scale morphology is necessary to sustain strong repulsion of liquids over time. However, while the water-catalyzed samples averaged a contact angle of 143° with water for well over 20 min, they only locally repelled hexadecane droplets, indicating an uneven coating. Therefore, NH_4OH is necessary not only for formation of a multi-scale structure with FS, but also for adequate attachment of FS to NyCo. In addition, the number of cures changed the wetting behavior of FS-treated NyCo when the samples were treated without base catalysis, but neither hydrophobicity nor oleophobicity of NyCo treated with FS in the presence of NH_4OH was significantly affected by the number of cures. Interestingly, the FS concentration, curing time, and the number of cures provide significant effect to the oleophobicity but not the hydrophobicity of FS-treated NyCo. Therefore, designing multi-scale geometric structure is required to improve hydrophobicity and oleophobicity of NyCo, and consequently this treatment can result in a highly hydrophobic and oleophobic material.

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