Biomimetic Superhydrophobic and Highly Oleophobic Cotton Textiles

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We report a biomimetic procedure to prepare superhydrophobic cotton textiles. By *in situ* introducing silica particles to cotton fibers to generate a dual-size surface roughness, followed by hydrophobization with polydimethylsiloxane (PDMS), normally hydrophilic cotton has been easily turned superhydrophobic, which exhibits a static water contact angle of 155° for a 10 μL droplet. The roll-off angle of water droplets depends on the droplet volume, ranging from 7° for a droplet of 50 μL to 20° for a 7 μL droplet. When a perfluoroalkyl chain is introduced to the silica particle surface, the superhydrophobic textile also becomes highly oleophobic, as demonstrated by a static contact angle of 140° and a roll-off angle of 24° for a 15 μL sunflower oil droplet.

Introduction

Millions of years of evolution in Mother Nature have perfected the design of desired surface wettability. For instance, many plant leaves (the lotus leaf being an outstanding example)[1] and insects (such as the water strider[2] and Namib desert beetle[3,4]) have "smartly" adopted a dual-size or even multiple-length-scale surface roughness to effectively generate superhydrophobicity. The superhydrophobic property is attributed to a smart combination of low surface-energy species and the peculiar topographic feature based on dual-size roughness. Due to potential applications in a variety of areas, there have been revived, extensive interests in superhydrophobic surfaces in the past decade.[5] Among others, superhydrophobic textiles have been successfully obtained by a number of different approaches.[6−10] For instance, Gao and McCarthy, according to a 1945 patent,[6a] grafted a silicone coating to a microfiber polyester fabric to render the fabric superhydrophobic,[6b] but the microfiber fabric (with a single fiber as small as 2−5 μm) needs to be tightly woven and this approach may not be suited to cotton textiles. Gold particles have been incorporated into cotton fabrics to induce a dual-size surface topology by Dong et al.,[8a] but obviously there is no chemical bond between the gold particles and cotton fiber. Similarly, particles have been introduced to various substrates to obtain water repellency by sol−gel methods.[9]

Inspired by the lotus leaf structure, we have recently prepared epoxy-based, polydimethylsiloxane (PDMS)-surface-modified, superhydrophobic films with a dual-size hierarchical structure originating from well-defined raspberry-like particles.[11] On this surface, the advancing contact angle for water is about 165° and the roll-off angle of a 10 μL water droplet is <3°. Here, we report the extension of this particle approach to cotton textiles, aiming at transforming hydrophilic cotton textiles into superhydrophobic and highly oleophobic textiles. Our particle-based approach is summarized as follows: silica particles with amine groups at the surface, covalently bonded to the cotton fibers, were *in situ* generated by either a one-step or two-step reaction; the amine groups were then used to hydrophobize the surface via the reaction with mono-epoxy-functionalized PDMS. For oleophobic textiles, a perfluoralkyl silane was used for the surface modification.

Experimental Section

Materials. A cotton textile was purchased from a local fabric store. Before chemical modification, a 16 cm^2 square piece of cotton textile was cleaned with water and ethanol before it was extracted with toluene to remove possible impurities. Tetraethylorthosilicate (TEOS) and 3-aminopropyl-triethoxysiloxane (APS) were purchased from Fluka and Merck, respectively. Monoglycidyl ether terminated PDMS (MGE-PDMS, average MW = 5000) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (R_f-Si) were obtained from Aldrich. Other chemicals were purchased from Merck and used without further purification.

***In Situ* One-Step Formation of Amine-Functional Silica Particles on Cotton Fibers.** The cleaned cotton textile was added to a solution of 25 mL of methanol, 75 mL of 2-propanol, 21 mL of ammonia solution, and a mixture of APS and TEOS in different ratios with a combined volume of 10 mL. The three APS/TEOS volume ratios used were 1/19, 1/9, and 1/4. The synthesis followed the traditional Stöber method.[12] The reaction mixture containing the cotton textile was mechanically stirred at 300 rpm for 6 h at room temperature. After the modification, the cotton textile was extensively cleaned with toluene to remove possibly physically adsorbed reactants and loose particles. To check if there are free amine groups on the

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Table 1. Water Contact Angles on Modified Cotton Textiles

sample ID	sample preparation[a]	static CA [°] (10 μL droplet)	roll-off angle [°] (10 μL droplet)
A	APS (no particles)	142 ± 3	36 ± 4
B	one-step: APS/TEOS = 1/19	142 ± 2	30 ± 5
C	one-step: APS/TEOS = 1/9	144 ± 1	22 ± 2
D	two-step: APS/TEOS = 1/4	149 ± 2	16 ± 1
E	particles from two-step reaction	155 ± 1	15 ± 1

[a] All samples were hydrophobized by MGE-PDMS.

surface, the ninhydrin test[13] was performed. The occurrence of a blue/purple color indicates the presence of amine groups in the sample.

Two-Step Formation of Amine-Functional Silica Particles. The above-described reaction was also performed in two steps: (1) silica particles were first formed on the cotton fibers in the absence of APS, and thus, the particle surface contained hydroxyl functionality and (2) the particle-containing cotton textile was added to an APS solution in toluene (5 mL of APS in 100 mL of toluene), and the mixture was mechanically stirred for 6 h at 60 °C. A similar cleaning procedure as above was performed afterward.

Surface Modification by PDMS and a Perfluoroalkyl Tail. The particle-containing cotton textile was further modified with the monofunctional MGE-PDMS by dipping the particle-containing textile in a MGE-PDMS solution in toluene (concentration: 5 vol %), and reacted for typically 12 h at 80 °C. MGE-PDMS can also be incorporated into the textile without prior dissolution in toluene. After the reaction, the excess PDMS was rinsed away with toluene. The surface fluorination was performed in a glove box. Similar to the PDMS modification, the particle-containing textile was dipped in a dry toluene solution containing the perfluoroalkyl silane (R_f-Si, 1 vol %) for 1 h at room temperature. The sample was then rinsed with toluene and dried.

A sonication test was performed to check how strongly the silica particles were attached to the cotton fiber. A small piece (2 cm × 1 cm) of sample D (Table 1) was immersed in an ethanol (about 30 mL) bath and sonicated for 30 min in a Branson 1510E sonicator operated at 70 W and 42 kHz. The sample was then dried prior to contact angle measurements.

Characterization Techniques. Contact angles and roll-off angles were measured with deionized water on a Dataphysics OCA 30 instrument at room temperature (~21 °C). All the contact angles and roll-off angles were determined by averaging values measured at 3−4 different points on each sample surface. Scanning electron microscopy (SEM) was performed on a Philips XL-30 ESEM FEG instrument (Philips, now FEI Co., The Netherlands) in high-vacuum mode operated at a 2 kV acceleration voltage. X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG-Escalab 200 spectrometer using an aluminum anode (Al Kα = 1486.3 eV) operating at 510 W with a background pressure of 2×10^{-9} mbar. Spectra were recorded using the VGX900 data system. All carbon 1s (C1s) peaks corresponding to hydrocarbon were calibrated at a binding energy of 285 eV to correct for the energy shift caused by charging. Spectra were acquired at a takeoff angle of 0° relative to the surface normal, corresponding to the probe depths of ~10 nm.[14] Thermogravimetric analysis (TGA) was performed with a TGA Q500 apparatus (TA Instruments) under oxygen at a flow rate of 50 cm^3 min^{-1}. A scanning rate of 20 °C min^{-1} was used with a temperature range from room temperature to 700 °C.

Results and Discussion

Chemical Modification of Cotton Textiles. The cotton textile was modified to incorporate chemically bonded silica particles as well as surface amine groups to the cotton fibers for further hydrophobization. It is, therefore, crucial to identify the presence of amine groups in the modified cotton textiles, which can be conveniently examined by the ninhydrin test. For both the one-step and two-step reactions in our procedure, when a ninhydrin solution was added to the modified cotton, the cotton color turned immediately blue or purple, indicating the presence of primary amine groups in the modified cotton.

We used XPS to characterize the cotton samples modified with only APS. Although XPS cannot give a full account of the chemical composition for cotton textile samples due to their rough surface, it does provide qualitative information on the chemical changes before and after the modification.[15] For the

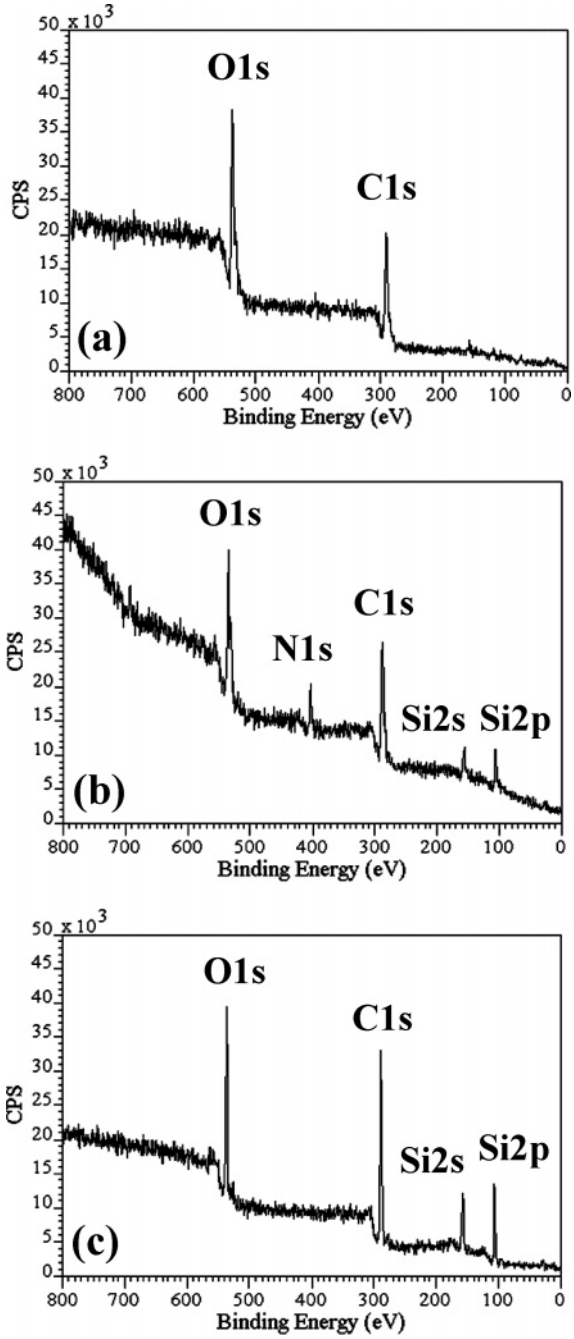

Figure 1. XPS spectra for (a) a cotton textile before modification, (b) the cotton sample after APS modification, and (c) the cotton sample after further modification with MGE-PDMS.

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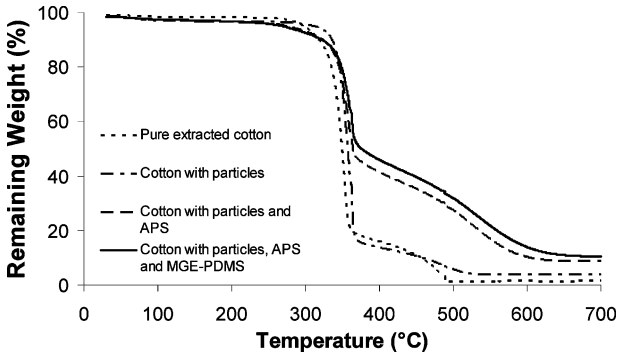

Figure 2. Weight loss for the cotton textile modified by the two-step procedure before and after each step of the modification by TGA.

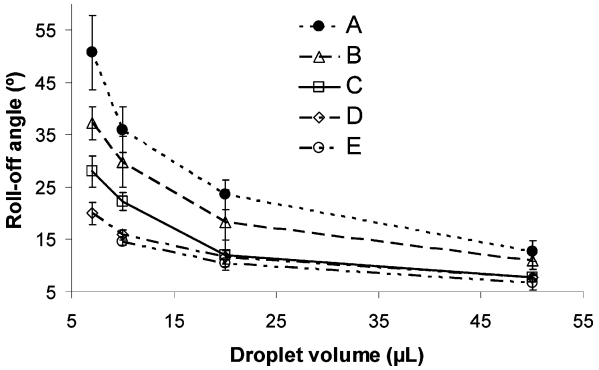

Figure 3. Roll-off angles of water droplets on modified cotton textiles as a function of droplet volume. For a description of the sample codes, refer to Table 1.

unmodified cotton textile, only peaks corresponding to C and O were observed (Figure 1a). After being modified by APS, three more peaks appeared (Figure 1b) at 400.5, 153.2, and 102.4 eV, which are attributed to N1s, Si2s, and Si2p signals, respectively, indicating the successful grafting of APS to the cotton fiber. The free amine group will be available for further modification. A preliminary quantitative analysis reveals that the atomic ratio of Si/O/C is about 1:1.7:4; the Si content appears to be significantly greater than the value assuming that a monolayer is formed during the APS modification. This is likely due to the formation of a 3D network layer from self-condensed APS in the presence of moisture,[16] resulting in a much higher Si content. After further surface modification with MGE-PDMS, only signals due to Si, C, and O were observed (Figure 1c), while the N1s peak disappeared completely. The observed Si/O/C ratio is 1.1:0.8:2, which is, considering the roughness of the cotton sample, reasonably close to the theoretical ratio of 1:1:2 for pure PDMS; this suggests that a layer of PDMS has covered the surface of the cotton fibers.

TGA was used to determine the remaining weights for the cotton sample after each step of the two-step modification procedure. For pure cotton prior to the modification, the remaining weight percentage is 1.5% after being heated to 700 °C in an oxygen atmosphere (the cotton fabric may not be pure cellulose), as shown in Figure 2. After silica particles are chemically grafted to the cotton fiber, this percentage increases to 4.0%. When APS is incorporated into the surface of the particles and, possibly, to the cotton fiber via the reaction with the remaining hydroxyl groups, the remaining weight percentage increases to 8.9% (the burning of the APS moiety would lead to SiO_2). This large increase, in comparison to the sample with only particles, implies that APS modification leads to more than a monolayer grafting of APS on the silica surface. Instead, a 3D-network layer[16] comprising self-condensed APS is formed (similar to the XPS results for the APS-modified sample without particles, as discussed above). A further increase of the remaining weight percentage to 10.4% was observed for the sample modified with PDMS (Figure 2), indicating the successful grafting of PDMS onto the particle surface.

Surface Wettability and Topology of Superhydrophobic Textiles. Surface wettability was examined by contact angle (CA) measurements. The pure cotton sample can be completely wetted by water, which is common and well-known for cotton textiles. The sample modified by APS (sample A, Table 1) and, subsequently, PDMS (i.e., without particles) was turned highly

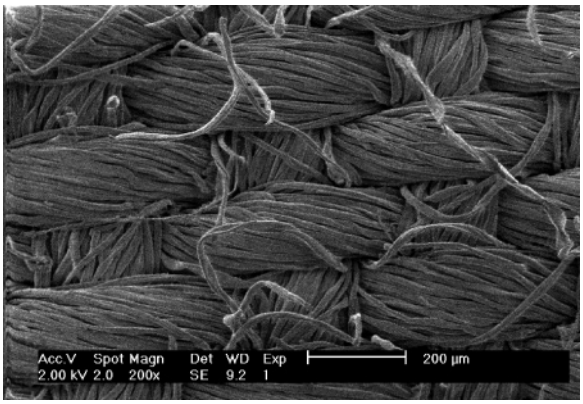

Figure 4. SEM image of the as-received cotton textile used in this study.

hydrophobic, with a water static CA of 142° and a roll-off angle of 36° (both for a 10 μL droplet). The hydrophobicity is further enhanced by incorporating silica particles into the modified textile samples (Table 1), as especially judged from the roll-off angle standpoint. The water static CAs range from 142° to 155° for a 10 μL droplet; even though these values are not super high, the modified cotton samples are completely water nonwettable.

When a water droplet sits on a hydrophobic cotton textile surface, the wetting behavior can be described by the equation from Cassie and Baxter:[17]

$$\cos \theta_{CB} = f_{ls} \cos \theta_0 - f_{lv} \quad (1)$$

where θ_{CB} is the observed water CA on a rough, porous surface, θ_0 is the intrinsic water CA on the corresponding smooth surface ($\theta_0 = 105°$ for a smooth PDMS surface), f_{ls} is the liquid/solid contact area divided by the projected area, and f_{lv} is the liquid/vapor contact area divided by the projected area. Equation 1 has been recently modified to account for the local surface roughness on the wetted area as follows:[18,19]

$$\cos \theta_{CB} = r_f f \cos \theta_0 + f - 1 \quad (2)$$

where f is the fraction of the projected area of the solid surface wetted by water (thus, we have $f_{lv} = 1 - f$) and r_f is the surface roughness of the wetted area. For the PDMS-modified cotton fiber in the absence of silica particles, the curvature of the cotton fiber renders $r_f > 1$, which, in comparison with a smooth wetted

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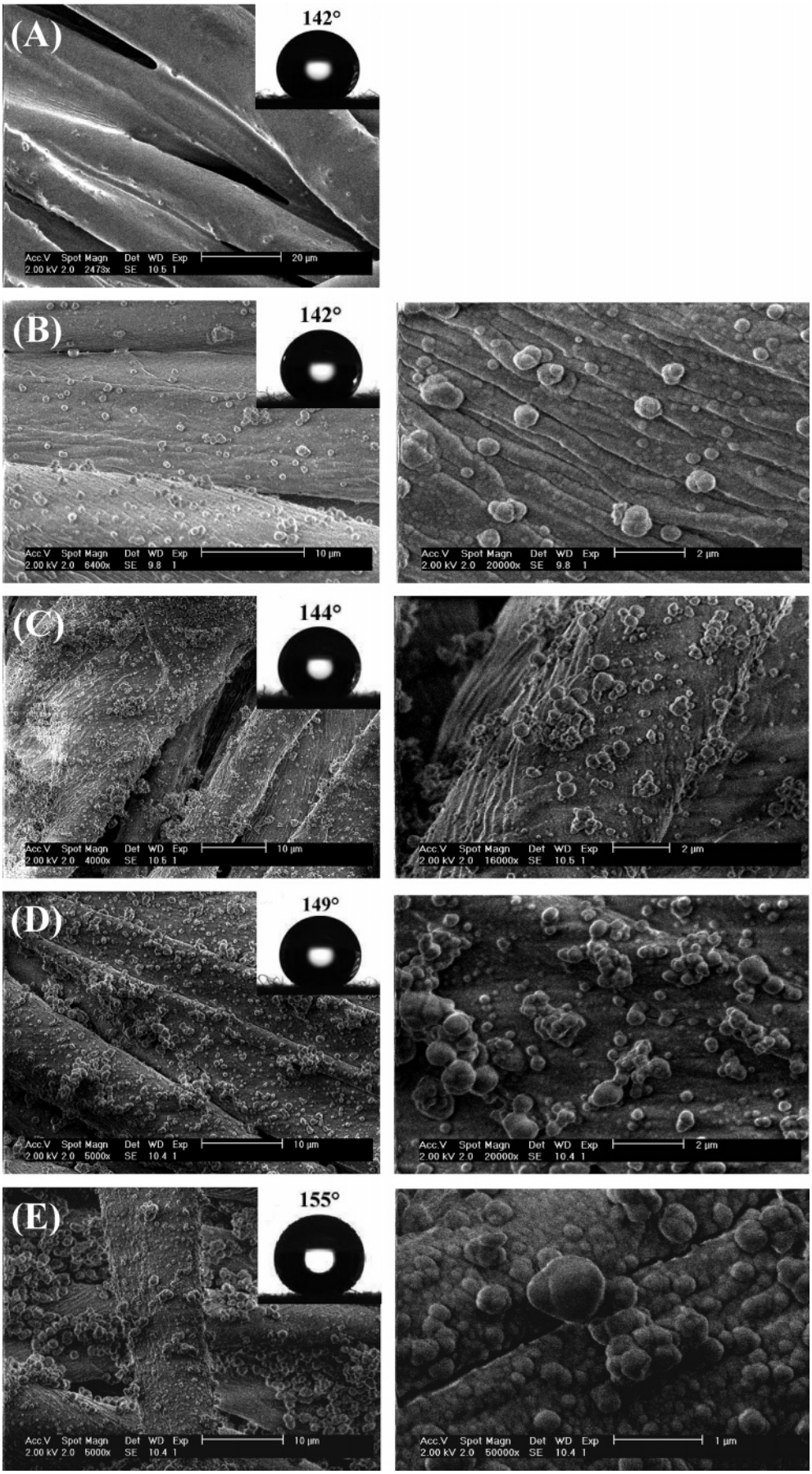

Figure 5. SEM images for particle-covered cotton textiles (without PDMS). The images on the right are higher-magnification ones for those on the left. Shown in the insets are the images of static water droplets (10 μL) on the respective particle-covered textiles modified by PDMS. For a description of the sample codes, refer to Table 1.

area, can enhance the surface hydrophobicity. When silica particles are chemically incorporated onto the cotton fiber surface in our study, r_f is further increased; the higher the area density of the silica particles (shown below by SEM) on the cotton fiber is, the greater r_f would become. Once r_f reaches a certain level, air may become trapped between silica particles underneath a water droplet, which would further enhance the surface hydrophobicity.

It should be noted that, due to the fibers sticking out from the cotton sample (as depicted in the optical image in the insets of Figure 5), the measurement of contact angles is often not straightforward, in terms of the difficulty of determining the baseline of the water droplet, which may in turn lead to possible underestimation of the contact angle data. Additionally, because the protruding fibers have some elasticity and can thus exhibit forces on the water droplet,[8a] it is also difficult to yield accurate values for advancing and receding water contact angles, so only static CAs for 10 μL water droplets are reported here (Table 1).

On the other hand, roll-off angles can be measured in a relatively accurate way. For a 10 μL water droplet, the roll-off angle decreases from 30° to 15° for samples B−E (all with silica particles; Table 1). For samples D and E, the roll-off angle for a 50 μL droplet is about 7°. In contrast, on a recently reported superhydrophobic woven structure,[19] the roll-off angle for a 500 μL droplet is 5°. When we use 500 μL water droplets, the roll-off angle on samples D and E is less than 2°. (A video clip in the Supporting Information shows the roll-off of a water droplet on a tilted superhydrophobic cotton textile, bringing away pencil graphite powder predeposited on the surface and leaving a clean path.) For the one-step modification procedure, it is obvious from Table 1 that the higher the amount of APS in the reaction mixture, the higher the water CA and the lower the roll-off angle. Sample E from the two-step procedure appears to have the best superhydrophobicity. We also checked the dependence of water roll-off angles on the droplet volume. As shown in Figure 3, for all the hydrophobic cotton textiles, the roll-off angle decreases as the water droplet size increases. This is as expected since, as the water droplet exceeds a certain size, its gravity would overcome the adhesion force between the cotton fibers and the water droplet. It is interesting to notice that, for sample E, we were unable to deposit a 7 μL water droplet on the textile surface and the water droplet always stuck to the needle, indicating that the adhesion force between the droplet and the textile surface is even lower than that between the droplet and the needle.

To find out how strongly the silica particles are attached to the textile surface, we subjected sample D to a sonication bath in ethanol for 30 min (ethanol completely wets the modified textile). The sample was then dried before CA measurements. We did not observe any significant change of its surface wettability: the static CA and roll-off angle of a 10 μL water droplet were 148 ± 1° and 17 ± 3°, respectively, which remain similar to the reported values in Table 1, indicating preliminarily that the silica particles are quite strongly linked (due to covalent bonding) to the cotton textile surface.

We used SEM to determine the topology of the cotton samples. The as-received cotton sample has a tightly woven, fibrous structure as shown in Figure 4. When the cotton sample was only modified by APS and followed by PDMS grafting, no significant change was observed by SEM (Figure 5A). On the other hand, when particles are incorporated into the cotton fibers, particles of sizes ranging from 500 nm to 2 μm are clearly visible (Figure 5B−E). With the chemical incorporation of silica particles into the cotton fibers, a dual-size surface structure has been conveniently generated. For the one-step modification procedure, the size of the particles does not change much (Figure 5B−D), but the particle population and distribution differ significantly. It appears that, as the APS/TEOS ratio increases, the silica particles become more numerous, and even nonspherical particles are formed, possibly due to the aggregation of smaller particles. For samples B and C, although the TEOS content is higher than that for sample D, the area density of particles is lower, possibly due to the formation of free particles (instead of being chemically connected to the cotton fiber). For the two-step procedure, the particle area density is the highest (Figure 5E) among the samples we have investigated, and the cotton fiber is quite densely covered by particles. The difference in the roll-off angles in Table 1 can be attributed to the different dual-size surface structure of the modified cotton samples. On one hand, the higher the area density of silica particles on the cotton fiber, the higher the water contact angle; on the other hand, a relatively high particle area density indicates that there would be less contact area between the water droplet and the particle-covered fiber surface, leading to a lower roll-off angle. This might be the reason that the cotton sample made via the two-step procedure demonstrates the lowest roll-off angles in the current investigation.

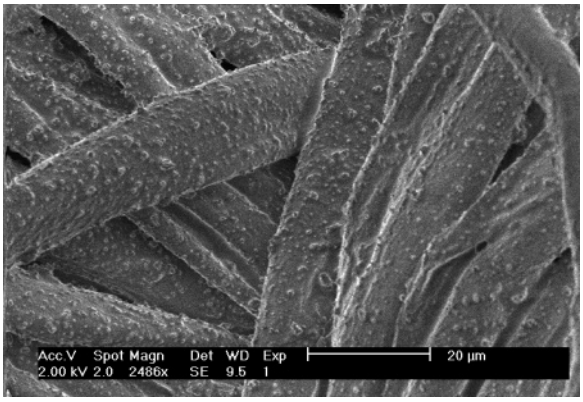

Figure 6. SEM image for a particle-covered cotton textile modified with PDMS (sample C in Table 1).

The surface of the textile after further modification by MGE-PDMS was also examined by SEM, as shown in Figure 6. It appears that both the silica particles and the cotton fibers are covered by a thin layer of PDMS, but the surface feature due to the incorporation of silica particles is preserved despite the PDMS surface grafting.

Highly Oleophobic Textiles with Surface Perfluorination. It is known that PDMS is hydrophobic but not oleophobic. To examine the oil repellency of the modified cotton textiles, a perfluoroalkylsilane (R_f-Si) was used for the surface modification. The water contact angle on this fluorinated cotton sample is similar to its PDMS-modified counterpart. On the other hand, the PDMS-modified sample can be completely wetted by hexadecane (a very hydrophobic liquid) and sunflower oil, which have surface tensions of 27.5 and 33.0 mN/m, respectively, at 20 °C. On the perfluorooctyl-modified cotton sample, the static CA for a 15 μL sunflower oil droplet is 140 ± 2° (the droplet image is shown in Figure 7a), and the roll-off angle for the same drop is 24 ± 2°. Obviously, the surface-fluorinated cotton sample has been turned highly oleophobic.

When hexadecane is used as the probe liquid, its static CA is about 135° for a 10 μL droplet (Figure 7b), significantly greater than that (typically 80°) on smooth perfluoroalkyl-modified surfaces.[20] However, even when the textile sample is turned upside down, the hexadecane droplet does not roll off of the textile. This behavior is similar to what has been termed "sticky

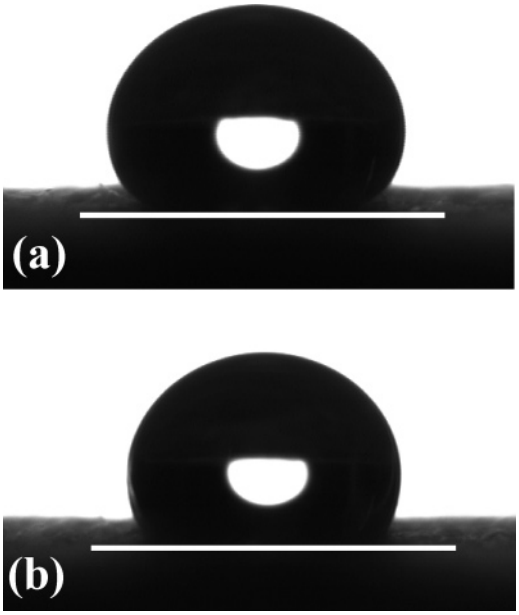

Figure 7. Images of (a) a 15 μL sunflower oil droplet and (b) a 10 μL hexadecane droplet on a perfluoroalkyl-modified, particle-covered cotton textile. The white lines are the droplet baselines from which the contact angles were determined.

superhydrophobic surface";[21] the difference is that our cotton sample demonstrates a sticky oleophobic behavior. This observation also indicates that, when a hexadecane droplet is deposited on the modified cotton sample, the wetting behavior may be in the Wenzel regime;[22] in contrast, when water or sunflower oil is used as a probe liquid, the liquid wetting reaches the Cassie regime,[17] where the roll-off of the liquid droplets becomes easy. For a topologically structured surface, the regime in which the wetting of a probe liquid is located depends on the surface tension of the liquid. We will report in the near future a modeling study on the wetting behavior of different probe liquids on a dual-size-structured surface.

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Conclusions

In summary, by *in situ* growing microsized silica particles to hydrophilic cotton textiles and using a hydrophobization step, we have generated a dual-size surface structure for the textiles and successfully turned them superhydrophobic. For a 10 μL water droplet, the static contact angle and roll-off angle are 155° and 15°, respectively. The area density of the silica particles needs to be high enough to achieve a low water roll-off angle. When the particle-covered textile is perfluorinated, the textile is also turned highly oleophobic.

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Supporting Information Available: Video clip showing the roll-off of a water droplet on a tilted superhydrophobic cotton textile, bringing away pencil graphite powder predeposited on the surface and leaving a clean path. This material is available free of charge via the Internet at http://pubs.acs.org.

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