Preparation of superhydrophobic surfaces on cotton textiles

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Abstract
Superhydrophobic surfaces were fabricated by the complex coating of silica nanoparticles with functional groups onto cotton textiles to generate a dual-size surface roughness, followed by hydrophobization with stearic acid, \textit{H}, \textit{H}, \textit{H}, \textit{H}, \textit{H}-perfluorodecyltrichlorosilane or their combination. The wettability and morphology of the as-fabricated surfaces were investigated by contact angle measurement and scanning electron microscopy. Characterizations by transmission electron microscopy, Fourier transformation infrared spectroscopy, and thermal gravimetric analysis were also conducted.

Keywords: superhydrophobicity, silica nanoparticles, cotton textiles, dual-size roughness

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Superhydrophobic surfaces have attracted great attention because of their potential applications in many areas \cite{1–9}. Among others, self-cleaning surfaces obtained considerable attention. A self-cleaning mechanism modeled after lotus leaves suggests that a combination of low-surface-energy materials and a specific surface topography based on a dual-size surface roughness are required to obtain a superhydrophobic surface. Micro- and nanoscale hierarchical structures have proven to be vital in generating the self-cleaning superhydrophobic property of a surface \cite{10}.

Many fundamental research studies on superhydrophobic surfaces are conducted on rigid solid substrates \cite{7, 9–12}, such as commonly used silicon wafers, glass slides and metal surfaces. These substrates might limit the practical application and large-scale production of superhydrophobic surfaces. Indeed the concept of superhydrophobicity was appreciated in the textile industry in the 1940s, but this appreciation has been forgotten \cite{13}. With the deepening of the research on superhydrophobic surfaces, textile substrates have been gradually paid attention again owing to the abundance and inexpensiveness of raw materials and easy large-scale area production. To date, a number of different approaches have been adopted to prepare superhydrophobic textiles \cite{13–21}. Gao and McCarthy \cite{13} grafted a silicone coating to a microfiber polyester fabric to render the fabric superhydrophobic according to a 1945 patent. However, the fabric with single fibers as small as 2–5 \textmu m should be tightly woven and this approach may not be suited to cotton textiles. Wang et al \cite{15} incorporated gold particles into cotton fabrics to induce a dual-size surface topology, but there is obviously no chemical bond between the gold particles and the cotton fibers, and this method is obviously expensive. Michielsen and Lee \cite{20} adopted a combination treatment of mechanical and chemical surface modifications, followed by further grafting of \textit{H}, \textit{H}-perfluoroctylamine or octadecylamine to poly(acrylic acid) chains on the pretreated nylon 6,6 fabric, to prepare superhydrophobic surfaces. However, this method relies on an expensive coupling agent, 4-(4, 6-dimethoxy-1, 3, 5-triazin-2-yl)-4-methylmorpholinium chloride. Hoefnagels et al \cite{18} reported the fabrication
of biomimetic superhydrophobic cotton textiles by either one-step or two-step reaction to in situ generate silica particles with amine groups on their surface, which were covalently bonded to the cotton fibers; the amine groups were then utilized to hydrophobize the surface via the reaction with mono-epoxy-functionalized polydimethylsiloxane. However, whether the reaction is one-step or two-step, 6 h mechanical stirring is required, which may cause damage to the textiles due to the entanglement problem, and therefore not suitable for industry production. Moreover, this method produces large particles with a diameter of about 1 µm as evidenced by their scanning electron microscopy images, which might hinder the softness and flexibility of natural cotton textiles. In addition to the approaches mentioned above, superhydrophobic cotton fabrics were prepared by the sol–gel coating of TiO$_2$ and surface hydrophobization by our group [21]. In this work, adopting the traditional textile finishing process, we have prepared superhydrophobic cotton textiles with a dual-size hierarchical structure obtained by the complex coating of silica particles with functional groups on microscale natural cotton fibers followed by hydrophobization with stearic acid, 1$H$, 1$H$, 2$H$, 2$H$-perfluorodecyltrichlorosilane (PFTDS) or their combination, as illustrated in figure 1. First, as-received cotton textiles are dipped into amine-functionalized silica particle solution and nipped by a padder. After repeating the process of dip and nip two times, the textiles are dried and again dipped into epoxy-functionalized silica particle solution and nipped by the padder. This process is also repeated two times, and the textiles are dried. During drying, reactions occurred between epoxy and amine groups, thus making the silica particles form a robust layer on the cotton fibers and leave the outer surface of the fiber full of epoxy groups available for further surface grafting. Then, stearic acid, PFTDS or their combination is grafted onto the rough surface to obtain a superhydrophobic property, as described in our previous work [21].

2. Experimental procedure

2.1. Materials

A white pure cotton textile, which was purchased from a local fabric store, was cleaned with deionized water and ethanol before it was dried for use. Tetraethylorthosilicate (TEOS), stearic acid, toluene, acetone, aqua ammonia (25–28%), methanol, and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. 3-aminopropyl-triethoxysiloxane (APTS, 98%), 3-glycidoxypropyl-trimethoxysilane (GPTMS, 98%), and PFTDS were purchased from Aldrich. All chemicals were used without further purification.

2.2. Preparation of amino-functionalized SiO$_2$ and epoxy-functionalized SiO$_2$

Monodispersed silica particles were prepared by polymerization of TEOS according to the Stöber method [22, 23], and the functionalization of SiO$_2$ was conducted according to the previous report [23]. Briefly, a mixed solution of 12 ml of TEOS and 80 ml of methanol was added dropwise under magnetic stirring to a flask containing 30 ml of ammonia solution and 320 ml of methanol at room temperature (15°C). The stirring was continued for 3 h. One drop of the reaction solution was diluted by methanol and used to characterize the obtained bare SiO$_2$ particles by TEM. Then, the solution was divided equally into two parts. One part was used for amino functionalization, and the other part for epoxy functionalization. For amino functionalization, the reaction was followed by the addition of 0.5 ml of APTS in 5 ml of methanol. For epoxy functionalization, the reaction was followed by the addition of 0.5 ml of GPTMS in 5 ml of methanol. Both reactions were continued overnight. Respectively, the functionalized nanoparticles were separated by centrifugation and washed by methanol three times. The obtained white powder was vacuum-dried at 50°C overnight.
Thus, amino-functionalized SiO$_2$ and epoxy-functionalized SiO$_2$ were obtained.

2.3. Preparation of superhydrophobic surfaces

Firstly, cotton textile was impregnated in an ethanol solution of 0.5 wt.% amino-functionalized SiO$_2$. Subsequently, the sample was passed through a two-roll laboratory padder giving a wet pick-up of 70–80%. After repeating this process two times, the textile was cured at 110°C for 1 h. Secondly, by substituting epoxy-functionalized SiO$_2$ for amino-functionalized SiO$_2$, the amino-functionalized-SiO$_2$-coated textile was further treated by the same method.

For hydrophobization of the textiles, stearic acid and PFTDS were used respectively or in combination. The treatment with stearic acid was conducted by impregnating the textiles in stearic acid solution, then padded and cured. Similarly, the treatment with PFTDS was conducted by impregnating the textiles in the PFTDS solution of toluene, then dried. For combination treatment, the samples were treated with stearic acid, followed by PFTDS. Details are described elsewhere [21].

2.4. Characterization

Contact angles (CA) were measured with a 5 µl deionized water droplet on a Dataphysics OCA 20 (Dataphysics, Germany) instrument at room temperature. All the contact angles were determined by averaging values measured at 5–6 different points on each sample surface. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 field emission scanning electron microscope. Thermogravimetric analysis (TGA) was performed with an SDT Q600 thermogravimetric analyzer (TA Instruments). Samples were heated at a ramp rate of 10°C min$^{-1}$ in air, with a temperature range from room temperature to 600°C. Fourier transformation infrared (FTIR) spectra were recorded with a Bruker VECTOR-22 IR spectrometer at a resolution of 2 cm$^{-1}$.

3. Results and discussion

3.1. Preparation of functionalized SiO$_2$ nanoparticles

By the Stöber method, it is very convenient to manipulate the particle size while maintaining a narrow size distribution in silica preparation. Figure 2 shows the TEM images of as-prepared bare and functionalized SiO$_2$ nanoparticles. All the TEM images show spherical particles with a size of about 70 nm. Bare and epoxy-functionalized SiO$_2$ nanoparticles are obviously distributed very appropriately, since silica particles are negatively charged [9]. While amino-functionalized particles present small clusters, which might be due to the interaction between the amino groups and negative charges on the bare part of the functionalized particles.

Figure 2. TEM images of (a) bare SiO$_2$, (b) amino-functionalized SiO$_2$ and (c) epoxy-functionalized SiO$_2$. 
3.2. Surface wettability and morphology

Surface wettability was examined by contact angle measurements. The results are shown in table 1. Pure cotton sample A0 can be completely wetted by water, owing to the highly hydrophilic property of cotton textiles. After the coating of functionalized silica particles, the observed CA is $70^\circ$, as shown by sample A8 in table 1, owing to the presence of $-\text{NH}_2$, epoxy and $-\text{CH}_2$ groups. Samples A1–A7 modified by stearic acid, PFTDS or their combination were turned highly hydrophobic, with a water static CA over $140^\circ$. Comparing sample A5 with sample A1, sample A6 with sample A3, sample A7 with samples A2 and A4, hydrophobicity is further enhanced by functionalized SiO$_2$ coating of the textile samples, as shown in table 1. The water static CAs range from 158$^\circ$ to 168$^\circ$ for a 5 $\mu$l droplet on the textiles treated by SiO$_2$ coating and hydrophobization, and the samples are completely water nonwettable, showing superhydrophobicity.

The wetting behavior of a water droplet on a hydrophobic cotton textile surface can be described by the equation of Cassie and Baxter [18, 21, 24]:

$$\cos \theta_{CB} = f'_E \cos \theta_0 - f_W,$$

(1)

where $\theta_{CB}$ is the observed water CA on a rough, porous surface, $\theta_0$ is the intrinsic water CA on the corresponding smooth surface, $f'_E$ is the liquid/solid contact area divided by the projected area, and $f_W$ 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 [18, 20, 21, 25]

$$\cos \theta_{CB} = r_l f \cos \theta_0 + f - 1,$$

(2)

where $f$ is the fraction of the projected area of the solid surface wetted by water (thus, we have $f_W = 1 - f$) and $r_l$ is the surface roughness of the wetted area. Generally, the water CA on smooth surfaces cannot exceed 120$^\circ$ through tailoring surface chemistry [26, 27]. For the stearic acid- or PFTDS-modified cotton fiber in the absence of SiO$_2$ particles, the curvature of the cotton fiber renders $r_l > 1$, which in comparison with a smooth wetted area, can enhance surface hydrophobicity. When SiO$_2$ particles are incorporated onto the cotton fiber surface in our study, $r_l$ further increases; the larger the roughness of the SiO$_2$ coating on the cotton fiber is, the greater $r_l$ would become, thus the CA would be larger as shown in figure 3 with (a) versus (c), in which the sample in figure 3(c) is obviously smoother than that in figure 3(a) owing to the disappearance of the large physically adsorbed loose particles pointed by arrows in figure 3(a). The same results were also obtained by comparing figures 3(b) and (d). Once $r_l$ reaches a certain level, air may become trapped between SiO$_2$ particles underneath a water droplet, which would further enhance surface hydrophobicity.

SEM was used to determine the morphology of the surfaces on the cotton samples. The as-received cotton textile has a tightly woven, fibrous structure, as shown in figure 4(a). Our previous study [21] showed that when the cotton sample was only modified by stearic acid and PFTDS, no significant changes were observed by SEM, and the surface of the fiber was very smooth, as shown in figure 4(b). When treated with SiO$_2$ particles, the surface of the microscale cotton fiber showed SiO$_2$ clusters, as shown in figure 3(a), making the surface rough, thus generating a dual-size surface structure on the textiles. From the higher-magnification images in figures 3(b) and (d), the spherical silica nanoparticles are clearly observed to be similar to those in the TEM images in figure 2.

It should be noted that, owing to the fibers sticking out from the cotton sample, the measurement of contact angles is often not straightforward, as a result of the difficulty in determining the baseline of the water droplet, which may in turn lead to the possible underestimation of contact angle data [18, 21]. Additionally, because the protruding fibers show elasticity and can thus exhibit forces on the water droplet [15], it is also difficult to yield accurate values for advancing and receding water contact angles, so only static CAs are reported here, as shown in table 1.

Comparing sample A1 with sample A2 in table 1, it was observed that the combination treatment of stearic acid and PFTDS presents a larger CA than the PFTDS treatment, which is in accordance with our previous work [21]. This goal was to decrease the usage of PFTDS in surface hydrophobization for lowering the cost in industrial application.

It should also be noted that the CA of sample A1 was obtained after many attempts owing to its high superhydrophobicity. Figure 5 shows a series of images taken during ascend (from figure 5(1) to figure 5(5)) and descend (from figure 5(6) to figure 5(10)) the textile surface of

### Table 1. Water contact angles on treated cotton textiles.

| Sample ID | Amino-SiO$_2$ (wt%) | Epoxy-SiO$_2$ (wt%) | Steric acid (wt%) | PFTDS (vol%) | Static CA (°) |
|-----------|---------------------|---------------------|------------------|-------------|--------------|
| A0*       |                     |                     |                  |             |              |
| A1        | 0.5                 | 0.5                 | 0.5              | 0.5         | 168.2 ± 2.1  |
| A2        | 0.5                 | 0.5                 | 1                | 1           | 160.2 ± 1.2  |
| A3        | 0.5                 | 0.5                 | 1                | 1           | 155.4 ± 2.1  |
| A4        | 0.5                 | 0.5                 |                  | 1           | 158.2 ± 1.3  |
| A5        | 0.5                 | 0.5                 | 0.5              | 1           | 154.0 ± 0.5  |
| A6        | 1                   |                     | 1                | 1           | 142.1 ± 1.4  |
| A7        | 1                   |                     |                  | 1           | 153.0 ± 0.5  |
| A8        | 0.5                 | 0.5                 |                  | 1           | 70.2 ± 4.2   |

*Sample A0 stands for cleaned pure cotton textile.
Figure 3. (a) SEM image of sample A1, (b) higher-magnification image of (a), (c) SEM image of sample A1 after sonication for 30 min and (d) higher-magnification image of (c). Shown in the insets are the images of static water droplets on the respective samples. For descriptions of sample codes, refer to table 1.

Figure 4. (a) SEM image of as-received cotton textile and (b) higher-magnification image of (a).

Figure 5. Series of images taken during ascending (from (1) to (5)) and descending (from (6) to (10)) of textile surface of sample A1; these images are taken from video clips.

3.3. FTIR analysis

The IR spectra of samples A0, A2 and A3 are shown in figure 6. The spectrum of sample A0 exhibited O–H stretching absorption at around 3440 cm$^{-1}$, C–H
Figure 6. FTIR spectra of samples (a) A2, (b) A0 and (c) A3. For descriptions of sample codes, refer to table 1.

stretching absorption at around 2800–3000 cm$^{-1}$, and C–O–C stretching absorption at around 1056 and 1110 cm$^{-1}$. These absorptions are consistent with those of a typical cellulose backbone [28, 29]. For sample A3 hydrophobized with stearic acid, the new peak at 2850 cm$^{-1}$ and increased peak intensity at 2920 cm$^{-1}$ of $\text{CH}_2$ due to the C–H symmetric and antisymmetric stretchings respectively indicate the introduction of long-chain hydrocarbon. The peak intensity at 1110 cm$^{-1}$ markedly increases and becomes higher than that at 1060 cm$^{-1}$, which is caused by the introduction of Si–O–Si since the peak intensity at 1110 cm$^{-1}$ is lower than that at 1060 cm$^{-1}$ in the spectrum of pure cotton. After silica nanoparticle coating and PFTDS treatment, although the spectrum of the obtained sample A2 is similar to that of sample A3, the peak intensities at 2850 cm$^{-1}$ and 2920 cm$^{-1}$ are lower than those of A3, because the number of $\text{CH}_2$ groups in PFTDS is much smaller than that in stearic acid. Moreover, the peak intensity at around 3440 cm$^{-1}$ in samples A2 and A3 is higher than that in sample A0, which is mainly caused by the large number of hydroxyl groups on silica nanoparticles coated on the samples. These observations confirm chemically that the as-described treatments were conducted successfully.

3.4. Thermogravimetric analysis

Figure 7 shows the TGA curves of samples A0, A1, A3 and A8. For pure cotton prior to the modification, the weight loss percentage is 100% after heating to 600 °C in air atmosphere, indicating that all the textile substances were burned, as shown by curve a. Curve d shows that after the coating of amino- and epoxy-functionalized nanoparticles, the weight loss percentage is 96.4%, with 3.6% of the original weight remaining owing to the residue of SiO$_2$. Curve c shows that after the stearic treatment of the silica-coated cotton textile, the weight loss percentage increases to 97.3%, and curve b shows that after the combination treatment of stearic and PFTDS, this percentage increases to 97.9%. These observations confirm the coating of silica on the cotton textile and the grafting of stearic acid and PFTDS onto the particle surfaces.

3.5. Robustness of superhydrophobic surfaces

To determine how strongly the silica particles are attached to the textile surface, sample A1 was subjected to sonication in ethanol for 30 min according to the reported method [18] and dried before SEM and CA measurements. Figure 3(c) shows that the surface of the fiber becomes slightly smoother than that in figure 3(a) after sonication, owing to the lost of physically adsorbed loose particles. Accordingly, the CA decreases from 168° to 163°, as shown in insets. The higher-magnification image in figure 3(d) shows that the main body of the surface has no significant differences from figure 3(b), indicating preliminarily that the surfaces obtained are robust.

4. Conclusions

Superhydrophobic surfaces on cotton textiles have been successfully prepared. The incorporation of functionalized SiO$_2$ particles by the traditionally textile finishing method not only generates a dual-size surface roughness but also facilitates the further hydrophobization of the surfaces to achieve a superhydrophobic property. The present strategy offers the following advantages: simple fabrication, easy availability of raw materials, and large-scale area production of superhydrophobic surfaces. These advantages make the present strategy suitable for real applications.

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