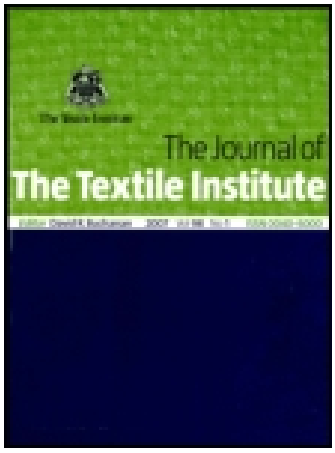


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# Transformation of hydrophilic cotton fabrics into superhydrophobic surfaces for oil/water separation

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In the present study, silica hydrosols were firstly prepared by water-based sol-gel method with the surfactant emulsification, using tetraethoxysilane as the precursor and ammonium hydroxide as the catalyst. Then, the silica hydrosols were applied to the cotton fabrics by dipping process, followed by the modification with (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane and heat treatment to prepare superhydrophobic cotton fabrics. The process resulted in $SiO_2$ nanoparticles covalently attached to the cellulose surface and fluorine-containing siloxane coupling agent which brought about an inherent microscale roughness and the superhydrophobic character. The investigation of oil/water mixture has been carried out using the as-prepared superhydrophobic cellulose fabric-based materials.

**Keywords:** composites; separation techniques; surfaces and interfaces; superhydrophobic; cotton fabrics; water/oil separation

## Introduction

Wettability is important for various kinds of solid surfaces (Wang et al., 2009; Wang, Li, & Lu, 2010). Superhydrophobic surfaces with a water contact angle (WCA) $>150°$ and a low sliding angle (SA) ($<10°$) have attracted considerable interest for both academic research and industrial applications in recent years, due to their self-cleaning properties (Li, Xie, Zhang, & Wang, 2007). The fabrication of superhydrophobic surfaces on textile substrates can provide the textile with water-proofing and self-cleaning properties, which makes higher potential application of textiles in specific domains. Thus, the fabrication of superhydrophobic textiles has been an attractive subject in the recent years (Shirgholami, Khalil-Abad, & Yazdanshenas, 2011).

Cotton is the most significant and also the purest source of cellulose fibers that normally occurs in nature. Because of its natural properties, cotton fabric is among the very popular textiles. However, cotton textiles are water absorbing and they would greatly benefit from utilizing hydrophobicity. Producing superhydrophobic surface on cotton fabric will guarantee its dryness and cleanness which are considered as desired features, in particular, on its outside facet (Berendjchi, Khajavi, & Yazdanshenas, 2011). Therefore, many efforts have been made to generate smaller scale structures to increase the hydrophobicity of the cotton fabrics. For instance, Gao and McCarthy (2006a) prepared superhydrophobic polyester fabric by using a simple patented water-repellent silicone coating procedure. But, the microfiber fabric with a single fiber as small as $\sim$2 μm needs to be tightly woven and this approach may not be suited to cotton textiles. Wang, Hu, and Dong (2007) successfully developed superhydrophobic surface on textiles by incorporating gold particles into cotton fabrics to induce a dual-size surface topology and subsequent modification with *n*-dodecanethiol. But, this method is no doubt an expensive one. Michielsen and Lee (2007) fabricated artificial superhydrophobic surfaces using mechanical and chemical surface modification of nylon 6, 6 woven fabric. Hoefnagels, Wu, de With, and Ming (2007) created superhydrophobic cotton fabrics by *in situ* growing microsized silica particles on cotton fibers to

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generate a dual-size surface roughness, followed by a hydrophobization step. But, large silica particles with a diameter about 1 μm might affect the softness and flexibility of natural cotton textiles. Usually, many of the used techniques involve multistep processes, expensive reagents, and special equipments, some of which are only applicable to small surfaces. Consequently, the practical application of superhydrophobic coatings on cellulosic textile materials is limited.

It is known that surface wettability is controlled by the chemical composition and surface roughness of solids. Roughened surfaces have been commonly obtained by introducing nanosize particles onto the surface. There are several kinds of inorganic nanosize particles such as $SiO_2$ (Xu, Zhuang, Xu, & Cai, 2011), $TiO_2$ (Goncalves, Marques, Pinto, Trindade, & Neto, 2009), and ZnO (Xu & Cai, 2008). On the other hand, the surface chemistry may be commonly modified by introducing some hydrophobic compounds through the surface condensation reaction (Gao & McCarthy, 2006b). In the present study, silica hydrosols were firstly prepared by water-based sol-gel method with the surfactant emulsification, using tetraethoxysilane (TEOS) as the precursor and ammonium hydroxide as the catalyst. Then, the silica hydrosols were applied to the cotton fabrics by dipping process, followed by the modification with (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (HFTMS), and heat treatment to create superhydrophobic cotton fabrics.

## Experiment

### *Materials*

Desized, scoured, bleached, and mercerized woven cotton fabrics (460 ends/250 picks) with warp yarns having 35 tex and filling yarns having 40 tex were used as the substrates. The weight per unit area of the fabric was 201 g/m$^2$. Sodium dodecyl benzenesulfonate (SDBS) and ammonium hydroxide ($NH_3 \cdot H_2O$, 28 wt%) were analytical reagents and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). HFTMS was obtained from Hangzhou Feidian Chemical Co. Ltd. (Hangzhou, Zhejiang, China).

### *Preparation of $SiO_2$ hydrosol*

$SiO_2$ hydrosol was synthesized by the hydrolysis and condensation of TEOS in isopropanol (IPA) solvent at the present of ammonium hydroxide (Xu et al., 2011). Firstly, 0.126 g of SDBS, 0.126 was added to 200 mL of water and stirred vigorously at 30°C for 90 min until a homogeneous emulsion formed. Then, 3.0 mL of $NH_3 \cdot H_2O$ was added to the mixture solution. Finally, 10 mL mixture solution of TEOS and IPA (1:1 in volume) was added dropwise to the above solution. The reaction was continued at 30°C for 4 h under stirring to form the $SiO_2$ hydrosol. By comparison with the traditional sol-gel reaction for the preparation of silica particles, water was used as solvent instead of alcohol in this study.

### *Preparation of the fluorine-containing siloxane solution*

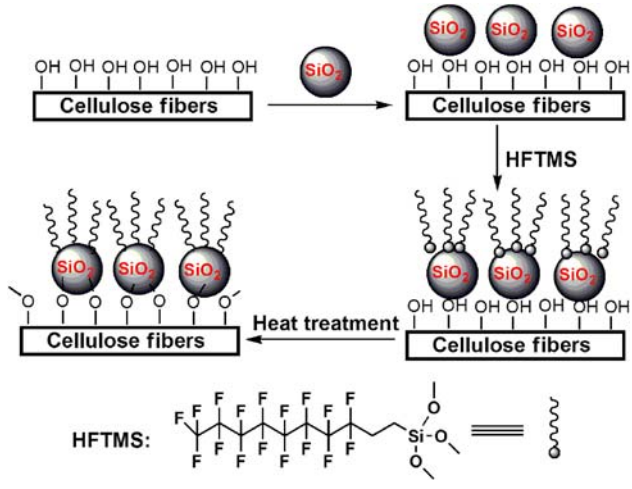
The 2.0 g of HFTMS was gradually added to 8.0 mL of alcohol. The solution was stirred for 30 min. The hydrolysis of HFTMS resulted in the formation of a fluorine-containing silanol solution.

### *Treatment of cotton fabrics*

The cotton fabrics were immersed in the $SiO_2$ hydrosol bath for 10 min, and then squeezed using an automatic padder with a nip pressure of 2 kg/cm$^2$. This process was repeated twice. The fabrics were then dried at 80°for 5 min, rinsed with water to remove residual surfactants, and dried at 80°C for 5 min again. The above treated cotton samples were immersed in the alcohol solution of hydrolyzed HFTMS for 12 h at room temperature. Afterwards, the cotton fabrics were air dried and then cured at 100°C or 150°C for 10 min in an oven to investigate the effect of temperature on the hydrophobicity.

### *Characterization*

Dynamic light scattering (DLS) measurements were performed in aqueous solution using a HORIBA Zetasizer apparatus (LB-550 V) equipped with a 5.0 mW laserdiode operating at 650 nm at room temperature. The measurements were conducted in quintuple. The results presented are the average data. The




Scheme 1. Formation of superhydrophobic surfaces on cellulose fibers.

surface morphologies of the cotton fabrics were examined by scanning electron microscopy (SEM) (JSM-5600LV, JEOL, Tokyo, Japan, operating at 10 keV) and field emission scanning electron microscopy (FESEM, Hitachi S-4800, Hitachi, Tokyo, Japan, operating at 3 keV). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 spectrophotometer (Nicolet, New York, USA) using a KBr pellets for samples. The hydrophobicity was characterized by the WCA measurements. The WCA measurement was carried out on an OCA40 contact angle system (Dataphysics, Berlin, Germany) using a 5 μL water droplet at ambient temperature. Ten readings were averaged to obtain one representative WCA for each sample.

## Results and discussion

In this study, the method employed is described in Scheme 1: first, a sheet of cotton fabric is cleaned by ultrasonic washing in ethanol and water, respectively, and then dried at 60°C in a vacuum oven for 1 h. Second, the cotton fabric is placed in a silica hydrosol for a set time. The $SiO_2$ nanoparticles are absorbed onto the cotton fibers' surface and penetrated into the fibers, due to the porous property of the fibers. The average particle size of the $SiO_2$ nanoparticles is around 50 nm which is measured by DLS. Next, the cotton fabric is withdrawn from the silica hydrosol solution and dried at 80°C in a vacuum oven. Third, the cotton fabric is further reacted with HFTMS to enhanced the hydrophobicity. Then, the cotton fabric is washed with water carefully to remove the excess



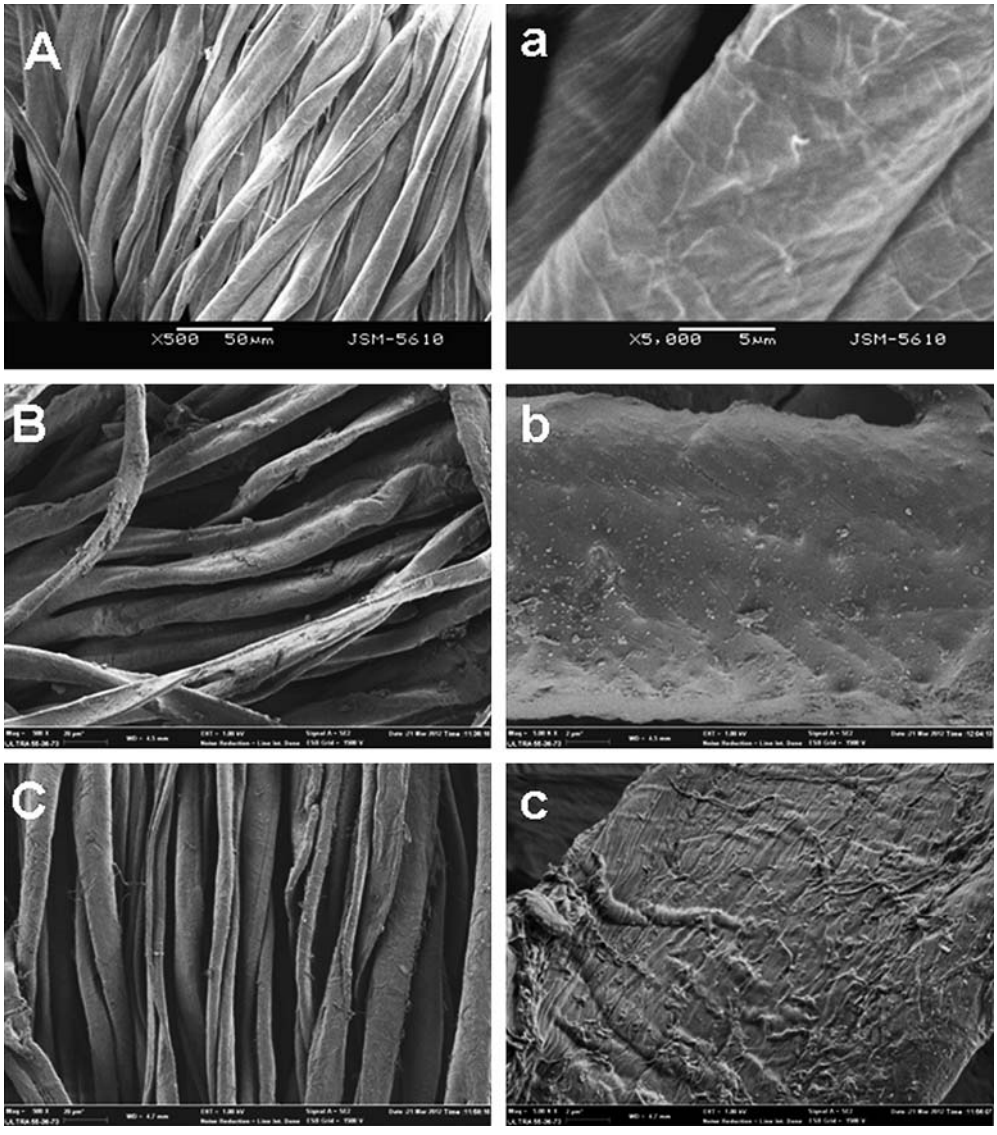



Figure 1. SEM images of (A, a) the pristine cotton fabric, (B, b) the cotton fabric coated by the silica hydrosol, and (C, c) the cotton fabric coated by the silica hydrosol followed by HFTMS modification and heat treatment at 150°C for 10 min.

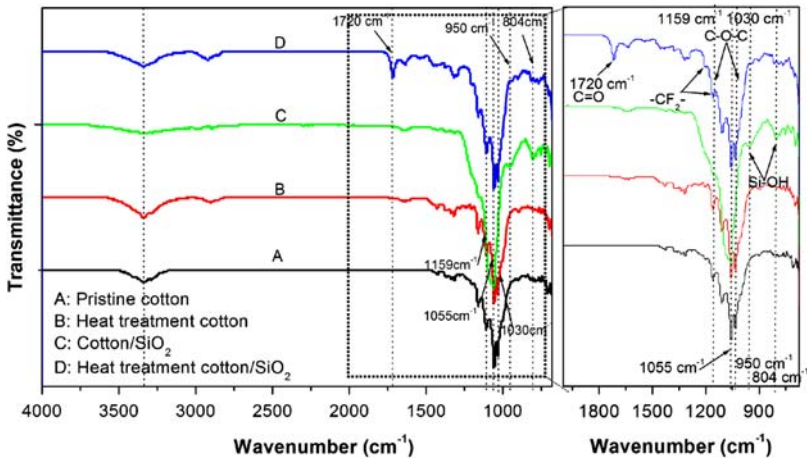



Figure 2. FT-IR spectra of pristine cotton (A), pristine cotton with heat treatment at 150°C for 10 min (B), cotton covered by $SiO_2$ nanoparticles with heat treatment at 150°C for 10 min (C), and the cotton fabric coated by the silica hydrosol followed by HFTMS modification and heat treatment at 150°C for 10 min (D).



reagents. Finally, the cotton fabric is treated in an oven at 150°C for 10 min. Subsequent polycondensation of Si–OH results in a nanoscale silicone coating tightly attached to the surface.

In an effort to get precise information of the nanocoating, the as-prepared cotton fabric examined by SEM. Figure 1(A) and (a) clearly show the furrows and fibrils on the pristine cotton due to the inherent characteristic of the cotton fiber. From Figure 1(B), the silica nanoparticles are covered on the surface of cotton fiber that treated by silica hydrosol alone and the cotton fiber shows relative higher roughness. From the higher magnification SEM image (Figure 1(b)), it can be observed that the silica nanoparticles were covered on the surface of cotton fabrics. The uniform distribution of $SiO_2$ nanoparticles with the diameter of around 50–100 nm can be also founded from the image. The increasing of the diameter of the $SiO_2$ nanoparticles may be contributed to the aggregation during the squeeze process. As we all know, cotton fabrics are highly hydrophilic and can be completely wetted by water. When the cotton fabric is coated by the silica hydrosol without HFTMS modification, the cotton fibers were densely covered with the $SiO_2$ nanoparticles. Hydrolyzed HFTMS and heat treatment are chemically bonded with $SiO_2$ particles on the cotton fiber by surface condensation reaction, resulting in the formation of ceraceous matters with nanoparticles as shown in Figure 1(C) and (c). The Si–$OCH_3$ groups in HFTMS molecule are reactive sites and subjected to hydrolysis to form the Si–OH groups. The dehydration reaction, subsequently, takes place between the alkylsilanol and the hydroxyl groups on the surface of $SiO_2$ particles, leading to the incorporation of HFTMS onto the cotton fiber with rough surface. On other hand, dehydration reaction also can be occurred between the hydroxyl groups on cellulose, making the increasing of hydrophobicity.

The chemical modification of the cotton textile is confirmed by FT-IR analysis (Figure 2). The spectra of four samples exhibit O–H stretching absorption at around 3340 $cm^{-1}$, C–H stretching absorption at around 2800–3000 $cm^{-1}$, and C–O–C stretching absorption at around 1030 and 1159 $cm^{-1}$. These absorptions are consistent with those of a typical cellulose backbone, as shown in Figure 2(A) (Xue et al., 2008). The spectrum of the cotton fabric after heat treatment is similar to that of pure cotton fabric without heat treatment (Figure 2(B)). In the case of cotton fabrics/$SiO_2$ composites (Figure 2(C)), two new

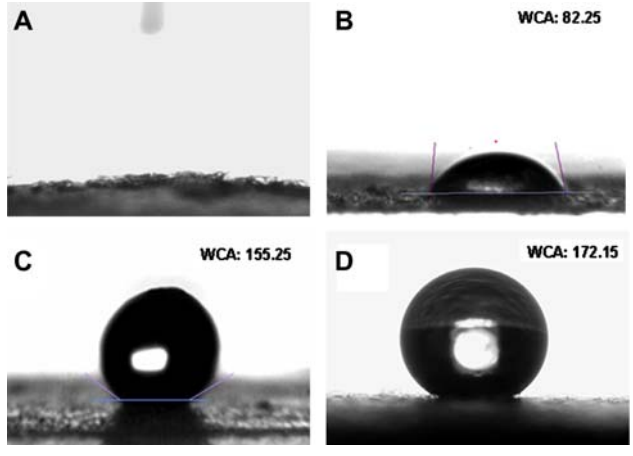



Figure 3. Water droplet (5 μL) images for cotton covered by $SiO_2$ nanoparticles (A), coated by silica hydrosols with subsequent HFTMS modification without heat treatment (B), coated by silica hydrosols with subsequent HFTMS modification and heat treatment at 100°C for 10 min (C), and coated by silica hydrosols with subsequent HFTMS modification and heat treatment at 150°C for 10 min (D).

absorption peaks located at 804 and 950 $cm^{-1}$, which can be attributed to the stretching vibrations of the Si–OH stretching (Xue et al., 2008). The peak relative intensity at 1159 and 1055 $cm^{-1}$ compared to that of pure cotton fabrics markedly decreases, which is caused by the introduction of Si–O–Si. After modification of HFTMS modification and heat treatment, a new absorption peaks located at 1720 $cm^{-1}$ as shown in Figure 2(D) which is attributed to the carbonyl stretching. Fluorocarbon functional group incorporation is indicated by the presence of the peaks at 1145 and 1211 $cm^{-1}$, which are due to $–CF_2–$ vibrations (Chung, Lee, & Choe, 2004). The typical absorption peaks of the Si–O–Si bonds of the siloxane compounds in the 1000–1130 $cm^{-1}$ region appear to be overlapped by the cellulose bands due to C–O bending modes.

As we know, cotton fabrics are highly hydrophilic and can be completely wetted by water. When the cotton fabric was coated by the silica hydrosol without HFTMS modification, the cotton fibers were covered with the $SiO_2$ nanoparticles. Because of the abundant hydroxyl groups on $SiO_2$ particles, a water droplet on the surface of the coated cotton fabric spreads instantly. So, the WCA of the cotton fabric coated by the silica hydrosol alone was supposed to be 0°, as shown in Figure 3(A). The cotton samples coated by silica hydrosols with subsequent HFTMS modification had the WCAs for a 5 μL water droplet with 82.25°, as shown in Figure 3(B). For the sample treated by $SiO_2$ nanoparticles, HFTMS modification, and heat treatment at 100°C for 10 min, the static contact angle (CA) for 5 μL droplet was $145° < \theta < 155°$ which demonstrated superhydrophobic property of the fabric. It is interesting to note that, further increasing the heat treatment temperature, the static CA can be improved to more than 170°. The condensation reactions between the hydroxyl groups, alkoxyl groups from HFTMS and hydroxyl groups from cotton or/and $SiO_2$ nanoparticles are more easily to react at higher temperature. In most cases, the silane is subjected to hydrolysis prior to the surface treatment. Following hydrolysis, a reactive silanol group is formed, which can condense with other groups, for example, silanol, hydroxyl, epoxy groups, and so on, to form siloxane linkages (Xue, Ishida, & Koenig, 1986). The content

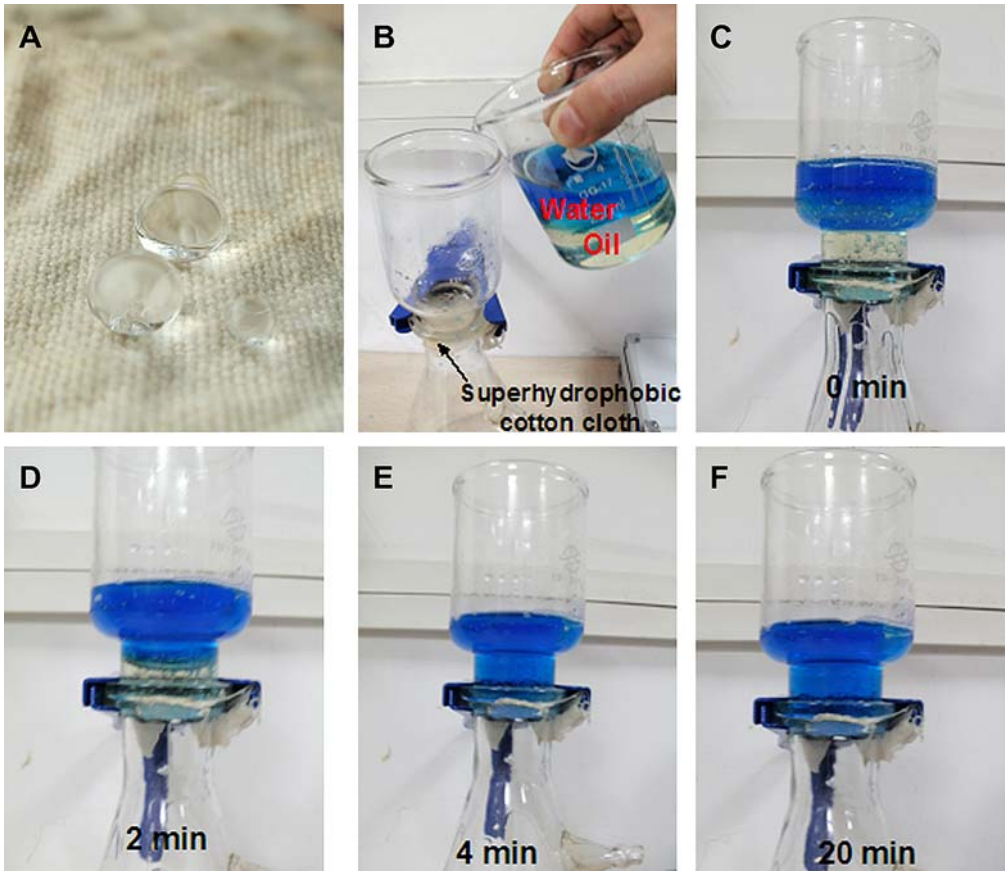



Figure 4. Optical microscope images of water droplets with different sizes on a superhydrophobic cotton cloth (A) and optical microscope images of a simple instrument for separation the mixture of oil and water (water dyed with methyl blue) (B–F).

of hydrophilic groups on the surface of cotton fabric decreases and hydrophobic property increases accordingly.

Beside the CA property, SA as one of the most important parameters determining the superhydrophobic state was also studied in this work. Obtained data clearly indicated that the SAs for the samples with heat treatment at different temperatures changed significantly. The superhydrophobic fabric with heat treatment at 100°C for 10 min showed a sticky property, so that 10 μL water droplet did not slide off even when the sample was turned to 90° or held upside down. However, in the case of superhydrophobic fabric with heat treatment at 150°C for 10 min, the SA is decreased significantly and reached to 18.5° ± 3.5°. The superhydrophobic behaviors observed in the "sticky", near "sticky" and "slippery" superhydrophobic fabric surfaces are expected to be modeled by Cassie's model (Cassie & Baxter, 1944; Shirgholami et al., 2011). The mobility switching of the water droplet is thought to be due to the abrupt change of the surface roughness (Li et al., 2007; Wang et al., 2007).

The optical image of water droplets on the surface of the as-prepared cotton fabric gives a direct demonstration of the superhydrophobic surface of cotton fabric, as shown in Figure 4(A). When a mixture of silicone oil and water (dyed with methyl blue for easy observation) was poured onto the superhydrophobic cotton cloth, only the oil could pass through the cloth and water droplets were held on the surface, as shown in Figure 4(B)–(F). This result implies that the special surface wettability enabled the modified filter cloth to separate oil–water mixtures with a high oil ratio (Wang et al., 2009, 2010). The water that flowed off the surface was collected and weighed. The separation efficiency was defined as the ratio of the weight of water collected to that initially added. The separation efficiency was >97% for silicone oil/water volume ratios ranging from 1:20 to 1:1.

## Conclusion

In conclusion, a facile way to transform very hydrophilic cellulose surfaces into extremely superhydrophobic ones has been developed based on absorption of $SiO_2$ nanoparticles with subsequent HFTMS modification and heat treatment technique. The process resulted in $SiO_2$ nanoparticles covalently attached to the cellulose surface and fluorine-containing siloxane coupling agent which brought about an inherent microscale roughness and the superhydrophobic character coupled with satisfactory durability. As expected, the approach is versatile and can be conducted on a variety of organic and inorganic substrates with hydroxyl group functionalized surfaces. The creation of superhydrophobic, cellulose fabric-based materials and transparency that has potential applications in oil–water separation area have also been investigated in this study.

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