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Fabrication of superhydrophobic/superoleophilic cotton for application in the field of water/oil separation

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ABSTRACT

Cotton with superhydrophobic and superoleophilic properties had been successfully fabricated for application in the field of oil/water separation by the combination of SiO_2 nanoparticles on cotton fiber surface and subsequent octadecyltrichlorosilane modification. The as-prepared cotton could be used to selectively absorb various common oils and organic solvents up to above 50 times of its own weight while repelling water completely. The absorbed oils were easily collected by a simple vacuum filtration, and the recovered cotton could be reused for several cycles while still keeping high absorption capacity. Moreover, the as-prepared cotton was simply spun into cloth, which not only could be tailored to the water-repellent clothing but also could be used in the oil/water separation filter system. The results presented in this work might provide a simple, low-cost and environment friendly approach for application in the field of water/oil separation.

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1. Introduction

With the frequently occurred water pollution caused by oil spillage and chemical leakage, the removal and collection of the organic contaminant from water has attracted great attention (Aurell & Gullett, 2010; Cheng et al., 2011; Lee & Rogers, 2013). The conventional methods of solving these problems include mechanical extraction, chemical degradation, combustion, and absorbent materials. Due to the economy and efficiency for removal and collection of oil, absorbent materials including inorganic mineral materials (Lee & Rogers, 2013; Teas et al., 2001), complex materials (Zhou & Chuai, 2010), and natural materials (Banerjee, Joshi, & Jayaram, 2006) etc., are considered a most desirable choice for the oil spill cleanup. Although these absorption materials have been widely studied and applied in practical applications for the removal and collection of spilled oil, there still exist some limitations such as environmental incompatibility, inadequate buoyancy, low oil absorption capacity, high cost, and poor reusability, and so on. Particularly, some materials absorb water and oil simultaneously, which indicates a poor hydrophobicity and reduces the oil/water separation selectivity and efficiency (Angelova, Uzunov, Uzunova, Gigova, & Minchev, 2011; Ceylan et al., 2009; Sidik et al., 2012). Therefore, the new oil-absorption materials with environmental compatibility, adequate buoyancy, high absorption capacity, low cost, good reusability, excellent selectivity and efficiency are significant for the development of the prevention and disposal of water pollution.

In recent years, some materials with the extreme wettability both superhydrophobicity (water contact angle higher than 150° and sliding angle less than 5°) and superoleophilicity (oil contact angle less than 5°) have attracted great interest for scientific community and potential applications in the area of oil/water separation because they only absorb oil while repelling water (Lee, Johnson, Drelich, & Yap, 2011; Song, Gaware, Rúnarsson, Másson, & Mano, 2010; Zhang, Wang, Wang, & Li, 2013; Zhang, Wang, Wang, Shi, & Li, 2012). As known from previous literature, the superhydrophobic property is attributed to the combination of micro/nano hierarchical structures of the substrate and the low surface energy of the surface (Li, Reinhoudt, & Crego-Calama, 2007; Zhang, Shi, Niu, Jiang, & Wang, 2008). On the basis of this principle, many different methods, such as laser/plasma etching (Song, Tang, Li, & Xiao, 2013; Yoon, Moon, Lyoo, Lee, & Park, 2009), phase separation (Zhao et al., 2005), layer-by-layer assembly (Jiang et al., 2005), lithographic patterning (Fürstner, Barthlott, Neinhuis, & Walzel, 2005), chemical vapor deposition (Ishizaki, Saito, & Takai, 2010), solution-immersion method (Li, Zhang, & Wang, 2008) and sol–gel method (Wang, Liu, et al., 2011) have been developed to design and fabricate superhydrophobic surfaces. Among these methods, the sol–gel method, generated micro/nano-structure onto the surface, has been found to be one particularly good technique for fabricating superhydrophobic coatings onto substrates because of its high efficiency and simplicity.

Cotton is a kind of favorable natural plant fiber material with various excellent characteristics such as softness, flexibility,

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environment friendly, and biodegradability. The fabrication of superhydrophobic/superoleophilic cotton-based materials could find potential applications in the field of oil/water separation. For instance, Wang et al. reported a simple drop-coating method for fabricating superhydrophobic and superoleophilic cotton textiles which can remove water in oil (Zhang et al., 2013). Zhou et al. prepared superhydrophobic and superoleophilic cotton fabrics for oil/water separation by a facile vapor phase deposition process (Zhou et al., 2013). In addition, a variety of materials, such as TPU film (Yang, Wang, Wang, Chen, & Chen, 2010), porous ceramic membrane (Su, Xu, Zhang, Liu, & Li, 2012), copper meshes (Pan, Wang, & Wang, 2008), graphene-based sponges (Nguyen, Tai, Lee, & Kuo, 2012), cotton fabric (Zhang & Wang, 2013) and polymer brushes (Tan, Hughes, Nagl, & Huck, 2012) have been prepared to separating oil from water (or water from oil). However, to the best of our knowledge, few studies have been reported regarding the fabrication of the cotton exhibiting superhydrophobicity and superoleophilicity simultaneously as a kind of oil-absorption material for the water/oil mixture separation with sol–gel method.

In this study, we presented a facile method to fabricate oil-absorption material based on superhydrophobic/superoleophilic cotton. The surface of cotton fibers was initially pretreated by NaOH aqueous solution, then coated with a film of SiO_2 nanoparticles via sol–gel process and subsequently modified with octadecyltrichlorosilane through a simple solution-immersion step. The as-prepared cotton could be used to selectively absorb various kinds of oils and organic solvents up to above 50 times of its own weight while repelling water completely. The cotton also showed good buoyancy on the water surface, and good reusability in oil/water separation cycle. The removal and the collection of the absorbed oils were easily achieved with the help of vacuum air pump. Moreover, the as-prepared cotton fibers could be simply spun into a piece of cloth, which could not only be tailored to the water-repellent clothing but also be used in the oil/water separation filter system. The results of this study provided an approach to fabricate superhydrophobic/superoleophilic cotton for application in the field of oil/water separation.

2. Experimental

2.1. Materials

Cotton was obtained locally. Tetraethoxysilane (TEOS, chemically pure), $NH_3{\cdot}H_2O$ (28%), glacial acetic acid (99.5%), anhydrous ethanol, toluene, *n*-hexane, chloroform, sodium hydroxide (analytical grade), methylene blue and Sudan III were obtained from Tianjin Kaitong Chemical Reagent Co, China. Gasoline, diesel and soybean oil came from the local market, Harbin, China. Octadecyltrichlorosilane (OTS) used for surface hydrophobic modification was purchased from New Jersey. Deionized water was self-made. All of the chemicals were used as received without further purification.

2.2. Pretreatment of the cotton

First, the cotton was ultrasonically washed with deionized water three times, and then put into a beaker containing 2% NaOH aqueous solution. Second, boiling the solution in the beaker for 10 min. Third, the cotton was washed several times with deionized water until the pH level of filtrate reached neutrality. Finally, the pretreated cotton was dried at 50 °C for 24 h.

2.3. Preparation of SiO_2 nanoparticles on the cotton fiber

The SiO_2 nanoparticles were prepared on the cotton fiber by a sol–gel process. In detail, the pretreated cotton was immersed into the mixture solution of 45 mL ethanol, 5 mL TEOS, 5 mL deionized water. Then, 5 mL $NH_3{\cdot}H_2O$ used as the catalyst was added dropwise into the mixture at room temperature under magnetic stirring (400 rpm) for 0.5 h (a homemade porous polyethylene baffle was used to separate the cotton from the magneton, for the purpose of preventing the nonuniform growth of nanoparticles aroused by the magnetic stirring).

After that, the cotton coated with SiO_2 nanoparticles was removed and washed by anhydrous ethanol for three times, blown to dry by N_2 and dried in a vacuum oven at 50 °C for 12 h eventually. SiO_2 nanoparticles synthesized on the cotton fibers by the above method are hydrophilic, with hydroxide groups on the SiO_2 nanoparticles surface.

2.4. Modification of SiO_2 nanoparticles coating on the cotton fibers

The surface modification of SiO_2 nanoparticles coating on the cotton fibers was performed by a self-assembly of OTS monolayer. First, the OTS ethanol solution was prepared by magnetic stirring the mixture of the 100 mL anhydrous ethanol, 2 mL OTS, 0.25 mL H_2O, 0.05 mL glacial acetic acid at room temperature for 4 h. Then, the cotton sample coated by SiO_2 nanoparticles was immersed into the OTS ethanol solution. The modification was maintained at 60 °C for 4 h. The resulting cotton was washed several times with anhydrous ethanol, and dried in a drying oven at 60 °C.

2.5. Characterizations

The geometric microstructures of cotton fibers were characterized by using scanning electron microscopy (SEM, FEI QUANTA200). The elemental composition of resulting cotton fiber surface was determined by Fourier transform infrared spectroscopy (FT-IR, Magna-IR 560, Nicolet) and X-ray photoelectron spectrometer (XPS, PHI Thermo Fisher Scientific Company Quantera), respectively. The water contact angles (WCAs) were measured with 5 μL deionized water droplet at room temperature using an optical contact angle meter (Hitachi, CA-A), and the final WCA was determined by averaging the measurements taken from at least five different positions on cotton fiber samples which were adhered on the glass slide by double-sided adhesive tape.

2.6. Measurements of maximal oil absorption capacity

For purpose of investigating the maximal oil absorption capacity of the superhydrophobic/superoleophilic cotton for common oils and organic solvents, the experiments of oil absorption were carried out in the pure oils and organic solvents, and the final maximal oil absorption capacity was determined by average value of 5 times experiments. Compared with the superhydrophobic/superoleophilic cotton, the oil absorption capacity of raw cotton before and after OTS treatment was measured by the same method. In typical absorption measurements, the cotton samples (1 g) were immersed in pure oil at room temperature, then left for a moment for saturated absorption, and finally weighted before draining for 15 s. The absorption capacity Q, defined as $Q = (M_{\text{saturated absorption}} - M_{\text{initial}})/M_{\text{initial}}$, was employed to measure how much oil was caught by the cotton samples.

2.7. Reusability

The superhydrophobic/superoleophilic cotton of absorbing oil was placed into a sand core funnel and drained under mild suction by a vacuum air pump for 5 min after weighting. Then the oil would be collected and the resultant cotton would be reused in the next absorption/collection cycle. The absorption/collection

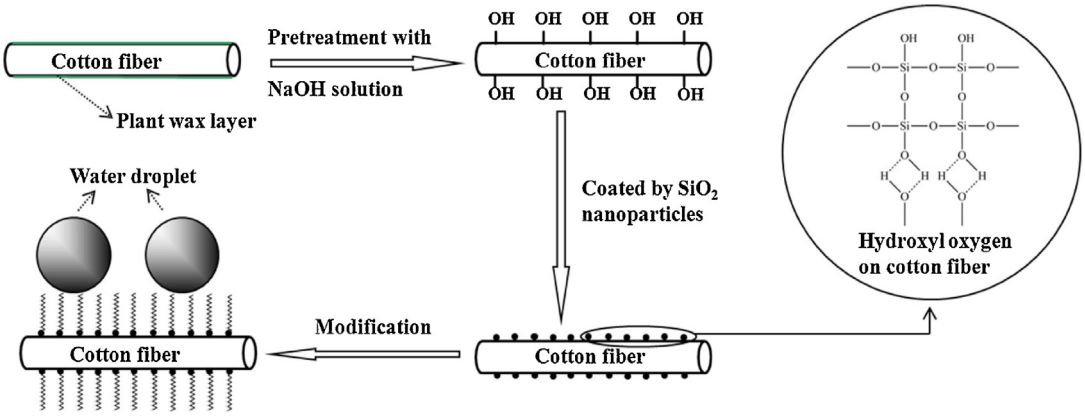

Fig. 1. Schematic illustration of the fabrication of superhydrophobic/superoleophilic cotton.

cycle was repeated for 10 cycles to evaluate the reusability of the superhydrophobic/superoleophilic cotton.

3. Results and discussion

3.1. Fabrication of superhydrophobic/superoleophilic cotton fiber surface and the morphology analyses

Fig. 1 describes the fabrication process of the superhydrophobic/superoleophilic cotton. In this study, the SiO_2 nanoparticles were coated on the cotton fiber in order to form a rough structure. The SiO_2 nanoparticles were prepared through a typical sol–gel process including the hydrolysis of TEOS and the condensation of the hydrolyzed SiO_2 species in the presence of ammonia catalyst. The sol–gel processes could be described as follows (Bae et al., 2009; Wang et al., 2011b):

(1) Hydrolysis

$$Si{-}[OC_2H_5]_4 + 4H_2O \rightarrow Si{-}(OH)_4 + 4C_2H_5OH$$

(2) Alcohol condensation

$$Si{-}(OH)_4 + Si{-}[OC_2H_5]_4 \rightarrow \equiv Si{-}O{-}Si\equiv + 4C_2H_5OH$$

(3) Water condensation

$$Si{-}(OH)_4 + Si{-}(OH)_4 \rightarrow \equiv Si{-}O{-}Si\equiv + 4H_2O$$

The surface of SiO_2 nanoparticles synthesized by this process has numbers of hydroxyl groups. Therefore, the hydroxyl groups on the cotton fiber play a key role for the preparation of superhydrophobic cotton fibers surface (Li et al., 2008; Vince et al., 2006). However, as shown in Fig. 2a, owing to the existence of the natural plant wax layer (Schmutz, Jenny, & Ryser, 1994), the surface of raw cotton fiber was smooth, which made SiO_2 nanoparticles not easy to attach to the fiber surface (Wang, Zheng, & Wang, 2012). Hence, the removal of plant wax layer would be very necessary. As shown in Fig. 2b, after the pretreatment of raw cotton, many longitudinal corrugations and interspaces appeared on the cotton fiber surface, suggesting that the natural plant wax layer of the raw cotton fiber had been removed and hydroxyl groups was exposed to make the cotton fiber more hydrophilic. Moreover, the generation of the corrugations and interspaces made the SiO_2 sol permeate the interspaces to generate SiO_2 nanoparticles easily (Lim & Huang, 2007). In these interspaces, the SiO_2 nanoparticles tightly adhered to the cotton fiber through the chemical bond interaction, which generated between the hydroxyl groups from cotton fiber and hydrolyzed silane. Fig. 2c shows that the single fiber was densely and uniformly covered by the SiO_2 nanoparticles and the arrangement of SiO_2 nanoparticles with diameter about 100 nm significantly strongly roughened the cotton surface. Finally, the cotton fiber coated by SiO_2 nanoparticles was modified by the OTS reagent, and the wetting behavior of this cotton surface obtained a great improvement with the WCA of 156°. By this OTS treatment, the hydroxyl groups produced from OTS hydrolysis reacted with the hydroxyl groups of SiO_2 nanoparticles and cotton fibers, and thus the long-chain hydrophobic alkyls were introduced on the cotton fiber surface. With the combination of fiber surface roughness and a layer of low surface energy OTS film, the cotton could not be wetted by water droplets and exhibited the property of superhydrophobic.

3.2. The wettability of superhydrophobic/superoleophilic cotton

For the purpose of reflecting the hydrophobic and oleophilic effect of the as-prepared cotton, the surface wettability of raw, pretreated and as-prepared cotton was investigated, as shown in Fig. 3(1). When the red-colored oil droplets dripped on the three kinds of cotton, it was quickly absorbed and the contact angel was almost 0°, indicating the superoleophilicity of three kinds of cotton samples. The blue-colored water droplets on the raw cotton showed water contact angle was 78° (Figs. 2a and 3(1)a), while the water droplet sunk quickly into the cotton fiber pretreated with NaOH, suggesting that natural plant wax layer was removed and hydroxyl groups were really created by the pretreatment of raw cotton. For the cotton fiber only modified by a self-assembly of OTS monolayer could achieve a maximal water contact angle about 124°, showing the hydrophobic property to some extent, but not superhydrophobicity. However, the cotton coated by the SiO_2 nanoparticles with subsequent hydrophobization showed the water contact angle of 156°, as shown in Figs. 2d and 3(1)c, which was much larger than the raw cotton, indicating that the hydrophilic raw cotton had been changed to superhydrophobic cotton by the treating processes.

When the raw cotton and superhydrophobic cotton were put on the water surface, the raw cotton sank beneath the water surface, on the contrary the superhydrophobic cotton floated on the water surface, as shown in Fig. 3(2)a. When the superhydrophobic cotton was totally immersed into water by an external force, it appeared as silver mirror-like surfaces, as shown in Fig. 3(2)b. This optical phenomenon should be attributed to trapped air layer between the superhydrophobic cotton and water (Nguyen et al., 2012; Zhu, Pan, & Liu, 2011). When the external force was removed,

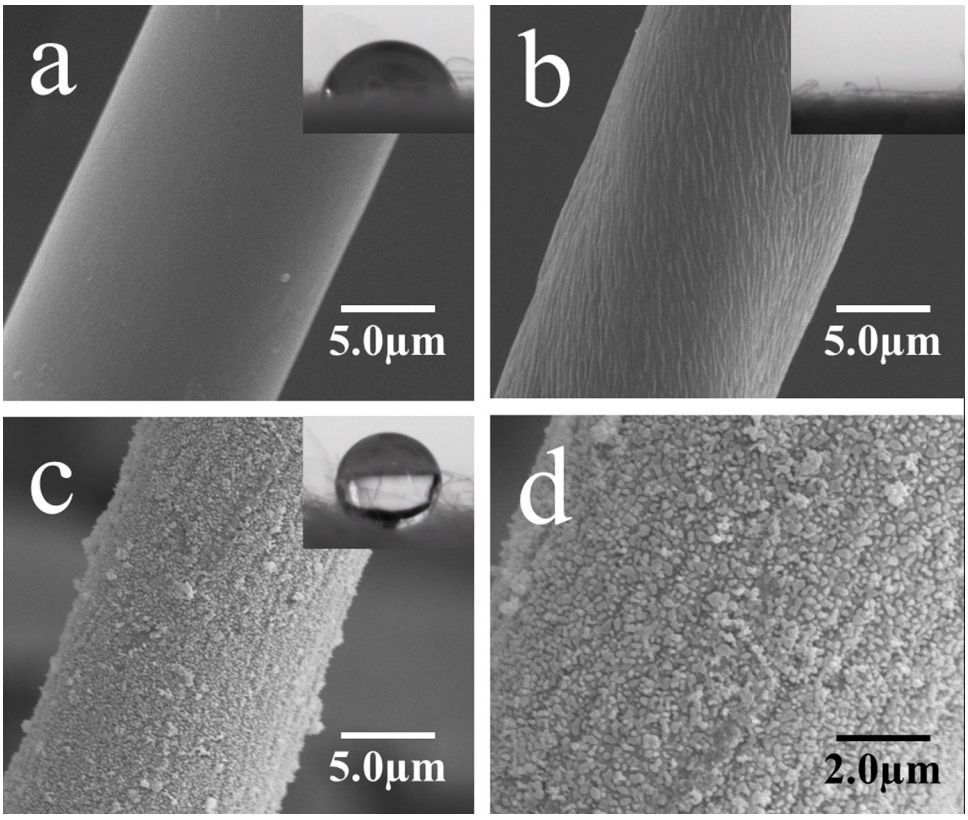

Fig. 2. SEM images of (a) raw cotton fiber, (b) pretreated cotton fiber and the superhydrophobic/superoleophilic cotton fiber at (c) low and (d) high magnification. Shown in the insets are the images of static water droplets (5 μL) on respective cotton samples which were adhered on the glass slide by double-sided adhesive tape.

the superhydrophobic cotton directly floated on the water surface, and no water uptake was measured subsequently weighing the cotton, indicating that the as-prepared cotton had very good buoyancy and water repellent. The combination of the trapped air layer and as-prepared cotton, which was lighter than water, was responsible for the good buoyancy.

3.3. Chemical composition analysis

The FTIR spectra of raw cotton and superhydrophobic cotton are shown in Fig. 4(1). In Fig. 4(1)b, the intensity of the peaks at broad absorption band 3335–3283 cm^{-1}, which are attributed to the stretching vibration peak of surface —OH, decreases obviously

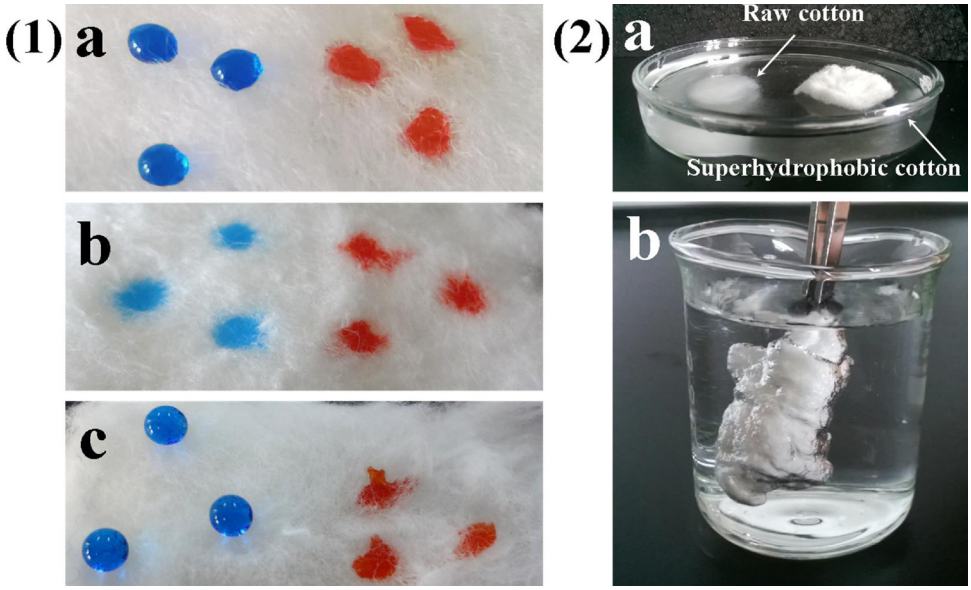

Fig. 3. Optical pictures demonstrating the wettability of the cotton samples. (1) Water droplets (dyed with methylene blue) and gasoline droplets (dyed with Sudan III) sitting on (a) raw, (b) pretreated and (c) superhydrophobic/superoleophilic cotton. (2) Top (a) raw cotton and superhydrophobic cotton was placed on the water surface. Raw cotton sinks beneath the water surface, while the superhydrophobic cotton floats on the water surface. Bottom (b) superhydrophobic cotton was immersed into water by an external force.

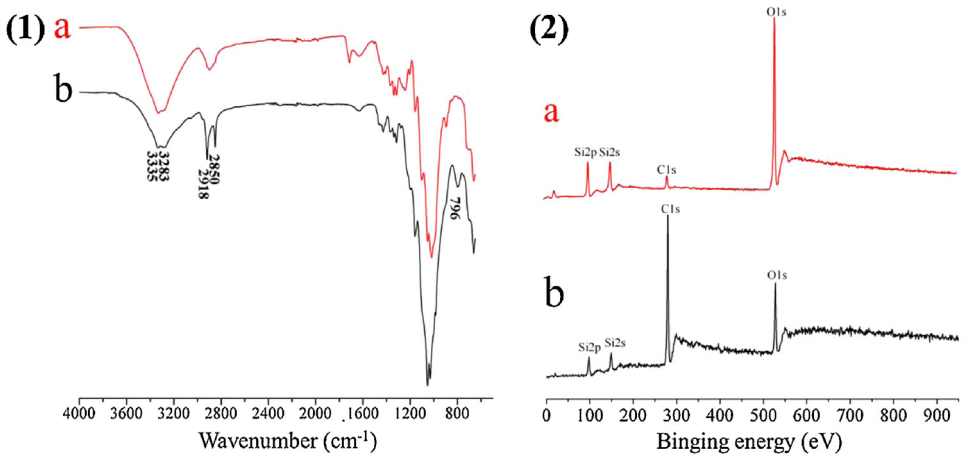

Fig. 4. (1) FTIR spectra of (a) raw, (b) superhydrophobic/superoleophilic cotton fabric surface. (2) XPS spectra of (a) the cotton fiber surface coated by SiO_2 nanoparticles without OTS treatment; (b) superhydrophobic/superoleophilic cotton fiber surface.

as compared with that of raw cotton. In the low frequency region, the absorption peaks at 796 cm^{-1} are assigned to the Si—O—Si asymmetric stretching, respectively (Hsieh, Wu, & Chen, 2010; Vinogradova, Estrada, & Moreno, 2006). In the high frequency region, there are two strong adsorption peaks at 2840–2910 cm^{-1} and 2910–2940 cm^{-1}, which stem from CH_3 and CH_2 asymmetrical stretching vibrations and symmetrical stretching vibrations, respectively (Wang, Piao, & Lucas, 2011; Wang, Li, & Xu, 2012). It indicates the existence of a long-chain alkyl group on surface of SiO_2 nanoparticles, which is caused by the OTS reagent (Zhang et al., 2012). These changes suggest that the total quantity of —OH groups was decreased and repellent SiO_2 nanoparticles were coated on the cotton fiber surface.

In addition, X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition of the cotton fiber surface coated by SiO_2 nanoparticles without OTS treatment and superhydrophobic cotton fiber surface as well. From Fig. 4(2), the peaks of Si2p, Si2s, C1s and O1s can be observed, and a remarkable increase of the C/Si/O ratio from 12.61/29.21/58.18 to 70.95/10.77/18.27. Obviously, the increase of C content further indicates the SiO_2 coating on cotton fiber surface have been successfully grafted with long-chain alkyl group from the OTS reagent.

3.4. Maximal oil absorption capacity of superhydrophobic/superoleophilic cotton for oils and organic solvents

The absorption capacities of the raw cotton, the raw cotton only modified by OTS reagent and as-prepared cotton for oils and organic solvents are shown in Fig. 5. The maximal oil absorption capacity of the raw cotton samples with and without OTS modification was basically the same, indicating that OTS modification only improved the hydrophobicity but did not enhance the lipophilicity on the smooth raw cotton surface. The absorption capacities of the as-prepared cotton for oils are 20–50 times of its own weight. Compared to the raw cotton and raw cotton modified by OTS reagent, the superhydrophobic/superoleophilic cotton exhibits a highest oil absorption capacity, suggesting that the superhydrophobic treatment is very useful for preparing a sort of oil sorbent with great oil absorption property.

Generally, the famous Young equation was used for describing the wettability of an absolutely smooth surface:

$$\cos\ \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

where σ_{sv}, σ_{sl}, and σ_{lv} are the interfacial tensions of the solid–vapor, solid–liquid, and liquid–vapor phases, respectively. To the actual surface, they are not absolutely smooth, thus Wenzel equation was applied to the contact angle θ_w of liquids on a rough homogeneous surface by modified Eq. (1)

$$\cos\ \theta_w = r\left(\frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}\right) = r\cos\ \theta \quad (2)$$

where r is the roughness factor defined as the ratio of the actual surface area of the rough surface to the geometric projected area, and it is always larger than 1. For purpose of further understanding the wettability of the superhydrophobic surface, the Cassie equation was employed to apply to heterogeneous roughness and low surface energy surfaces which exhibit superhydrophobic:

$$\cos\ \theta_c = f(\cos\ \theta + 1) - 1 \quad (3)$$

where f is the fraction of the solid surface contacting with liquid, the fraction of air in contact with contacting with liquid at the surface is $1 - f$, θ and θ_c represent the water contact angle on smooth and rough surfaces, respectively (Liu et al., 2013).

Consequently, according to the Wenzel equation and Cassie equation, the fabrication of a proper rough construction not only can make the hydrophobic surface to be more hydrophobic or even superhydrophobic, but also can turn a smooth oleophilic surface

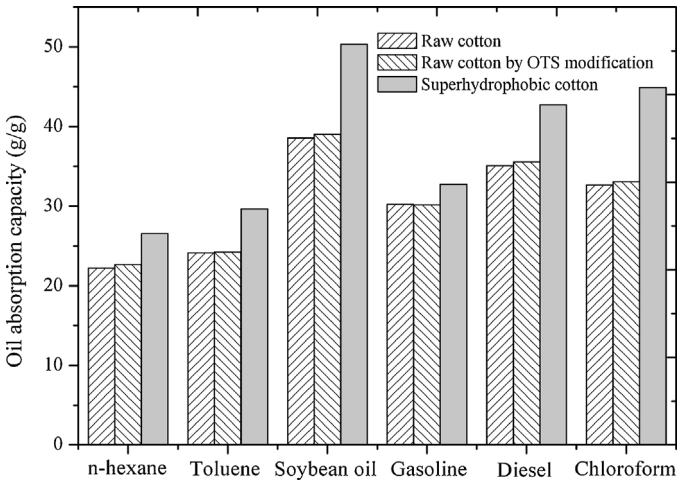

Fig. 5. Maximal oil absorption capacity of raw cotton, the raw cotton by OTS modification and the superhydrophobic/superoleophilic cotton for oils and organic solvents.

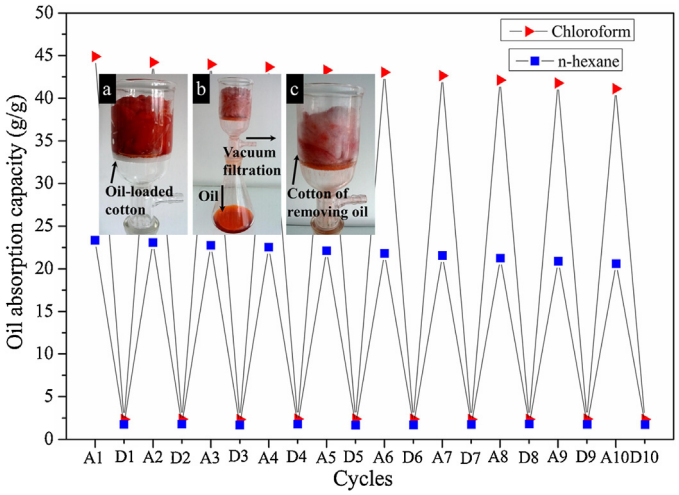

Fig. 6. Reusability of superhydrophobic/superoleophilic cotton in chloroform and *n*-hexane: A1–A10 = oil absorption cycle condition; D1–D10 = oil desorption cycle condition. Shown in the inset is the process of collect oil from oil-loaded superhydrophobic/superoleophilic cotton with the help of vacuum air pump.

to be a more oleophilic or even superoleophilic surface. In this study, through the fabrication of rough construction and subsequent modification by low surface energy reagent, the lipophilicity of raw cotton was remarkably improved. By comparison, oil could easily slip off from the smooth raw cotton fiber surface. This observation indicates the importance of surface roughness and low surface energy materials for the preparation of superhydrophobic/superoleophilic cotton.

3.5. Reusability

The superhydrophobic/superoleophilic cotton could be reused for absorbing the oils with high capacity and the absorbed oil could be recovered, which are significant features for practical application. In order to recover the absorbed oil and reuse the superhydrophobic/superoleophilic cotton, oil-loaded cotton was squeezed with the help of vacuum air pump, as show the inset of Fig. 6, and the cotton of removing oil was reused to the next absorption/collection cycle.

Fig. 6 shows the reusability change of the superhydrophobic/superoleophilic cotton for absorption of *n*-hexane and chloroform. There were a slight decrease of the maximal oil absorption capacity through the whole cycle process and the residual oil capacity for *n*-hexane and chloroform was always maintained in the scope of 2–3 g/g after every oil collection. Namely, the oil absorption capacity of superhydrophobic/superoleophilic cotton almost had no remarkable decrease after 10 absorption/collection cycles and more than 90% mass of absorbed oil could be thoroughly recovered by the vacuum filtration after every absorption/collection cycle.

When the raw cotton was pretreated with NaOH aqueous solution, the natural plant wax layer of the raw cotton fiber was removed and a lot of hydroxyl groups were exposed. Meanwhile, the surface of cotton fiber appeared many corrugations and interspaces, as shown in Fig. 2b. When the pretreated cotton sample was immersing in the SiO_2 sol, the SiO_2 sol permeated the corrugations and interspaces and the SiO_2 nanoparticles tightly adhered to the cotton fiber through the chemical bond, which generated between the hydroxyl groups from cotton fiber surface and hydrolyzed silane. Therefore, when as-prepared cotton was reused to absorb the oils, SiO_2 nanoparticles coated on the cotton fibers was firmly adhered to the surface of fibers and not easily fall off, indicating that the surface structure of as-prepared cotton was not easily changed after reutilization. So the as-prepared cotton has good reusability.

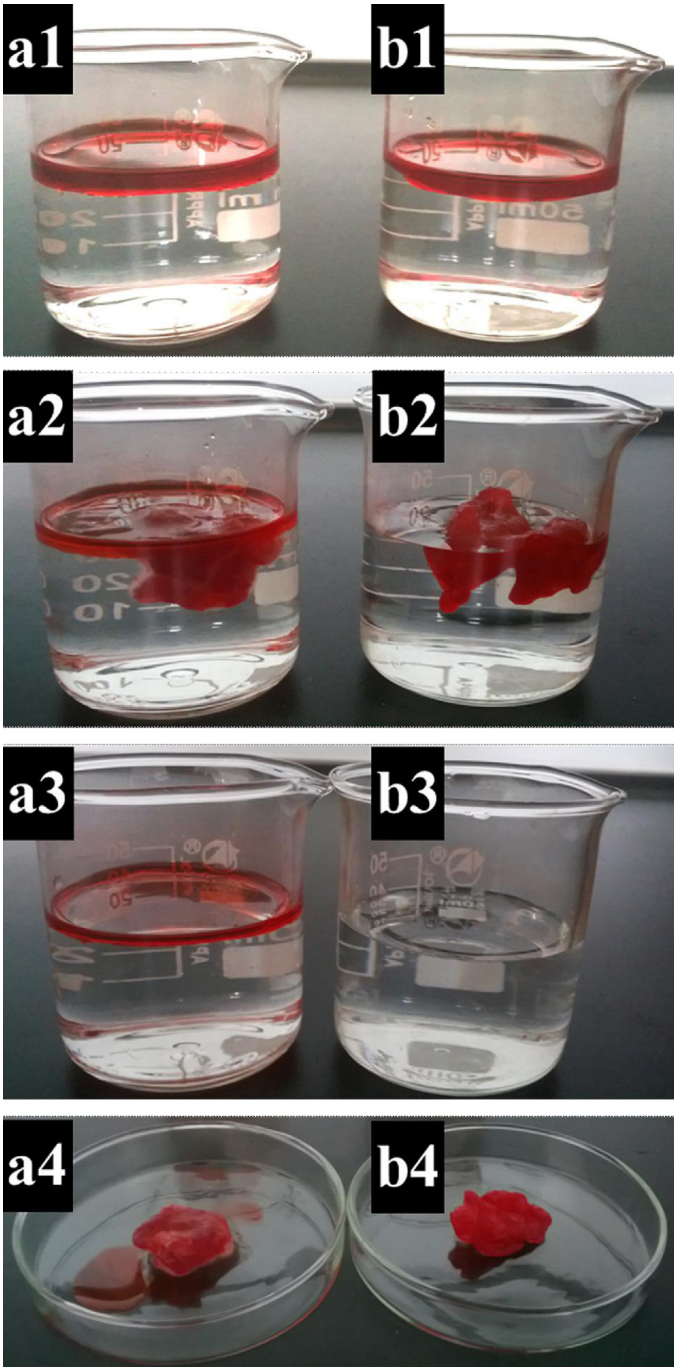

Fig. 7. Pictures for the cleanup of toluene (dyed with Sudan III) from water surface by the raw cotton (a) and superhydrophobic/superoleophilic cotton (b). (a1) and (b1): toluene was floating on water surface; (a2) and (b2): toluene was absorbed by raw cotton and superhydrophobic cotton, respectively; (a3) and (b3): water surface after taking away oil-loaded cotton samples; (a4) and (b4): the oil-loaded cotton samples were picked up on the watchglasses.

3.6. Application in water/oil separation

The separation of oil from water was carried out by putting the superhydrophobic/superoleophilic cotton into oil/water mixture. In order to intuitively exhibit the effect of oil absorption of the as-prepared cotton, the oil absorption experiment of raw cotton was conducted by the same parameters, and the optical images

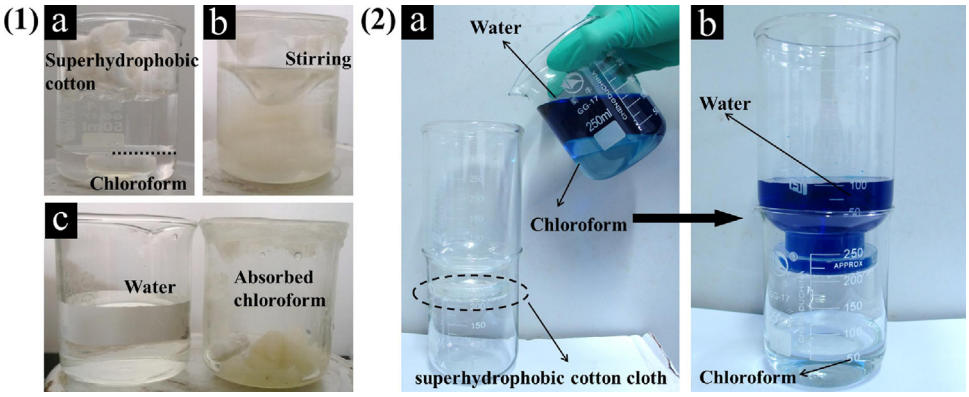

Fig. 8. (1) Absorption process of the superhydrophobic/superoleophilic cotton in chloroform/water mixture. A vortex stirring process was employed to absorb the chloroform submerged underwater. (2) Pictures of the as-prepared cotton cloth-based water/oil separation process of water and chloroform. The water was dyed with methylene blue for clear observation.

for the separation of toluene from the water surface by raw and as-prepared cotton are shown in Fig. 7.

As mentioned previously, the superhydrophobic/superoleophilic cotton could not be wetted and no water was absorbed when it was immersed into water. By placing the as-prepared cotton in the surface of oil/water mixture, the as-prepared cotton could energetically absorb and remove the oils floating on water surface. As shown in Fig. 7b2, we observed that the as-prepared cotton absorbed oil floated and moved freely on the water surface. Then, the oil was completely removed from the oil/water mixture by taking away the oil-loaded cotton from the water surface, and no obvious residual oil could be observed in the beaker, as shown in Fig. 7b3. In contrast, for raw cotton, it was difficult to thoroughly remove only 15 g/g oil from the mixture surface, and when the oil-loaded cotton was picked up, there was a very serious oil-dripping, as shown in Fig. 7a3 and a4.

To better verify the superhydrophobic/superoleophilic cotton's separation effect and practical application, Fig. 8(1) illustrates the detailed process of chloroform absorption by the as-prepared cotton. After cutting the superhydrophobic/superoleophilic cotton into small pieces, the pieces of the superhydrophobic/superoleophilic cotton were placed in the oil/water mixture. Then the beaker containing the superhydrophobic/superoleophilic cotton pieces and oil/water mixture was artificially shaken by an agitator, mimicking the motion of ocean waves (Choi et al., 2011). The results showed that the chloroform was completely absorbed into the as-prepared cotton pieces within a few seconds.

In addition, the superhydrophobic/superoleophilic cotton fiber could be spun into the cloth, which not only could be tailored to the water-repellent clothing but also could be used in the oil/water separation filter system. Herein, the superhydrophobic/superoleophilic cotton fiber was simply spun into a piece of cloth to test to effect of the separation of oil from water. Fig. 8(2) shows the images of the equipment for separation process, and the mixture with 50 mL chloroform and 100 mL water before and after separation through superhydrophobic/superoleophilic cotton cloth. In the superhydrophobic/superoleophilic cotton cloth-based filter device, the as-prepared cotton cloth was fixed on the filtering apparatus. As expected, while the mixture of chloroform and water (dyed by methylene blue) was poured onto the as-prepared cotton cloth surface, the chloroform freely penetrated the cloth, and then rapidly fell into the beaker underneath, whereas the water could not permeate through the cotton cloth and still retained on the cloth. It indicates that superhydrophobic/superoleophilic cotton cloth fabricated by our approach could separate oil from water availably, and this type of cotton offered a considerable application prospect for oil/water separation.

4. Conclusion

In summary, the cotton with superhydrophobic and superoleophilic properties was achieved by the combination of SiO_2 nanoparticles on cotton fiber surface and subsequent octadecyltrichlorosilane modification. The as-prepared cotton can be applied as a kind of oil-absorption material for the water/oil mixture separation. It exhibited excellent properties such as water-repellency, high oil absorption capacity, adequate buoyancy, good reusability and easy fabrication. The results of this study provided an approach to fabricate superhydrophobic/superoleophilic cotton for application in the field of oil/water separation.

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