Thiol-ene Click Chemistry Construct Superhydrophobic Cotton Fabric for High-efficiency Water-in-oil Emulsion Separation

Guihua Meng[†], Jiayu Yan[†], Jianning Wu, Weifang Zhang, Yixi Wang, Qian Wang, Zhiyong Liu*, and Xuhong Guo

School of Chemistry and Chemical Engineering, Shihezi University,
Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan,
Key Laboratory of Materials-Oriented Chemical Engineering of Xinjiang Uygur Autonomous Region,
Engineering Research Center of Materials-Oriented Chemical Engineering of Xinjiang Bingtuan,
Shihezi, Xinjiang 832003, China

Abstract: Water pollution severely effects human health and ecosystems. This paper presents a simple method of superhydrophobic cotton fabric fabrication for oil/water separation, We implemented thiol-ene reaction using 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) and *n*-dodecyl mercaptan (NDM). to synthesize low surface energy hydrophobic modifier. Superhydrophobic cotton fabrics demonstrated excellent superhydrophobicity, which makes them outstanding materials for continuous and simultaneous removal of insoluble and emulsified oils. Chemical composition, morphology, and hydrophobicity of these cotton fabrics were confirmed by FTIR spectra, scanning electron microscopy (SEM), and water contact angle measurements, respectively. Fabrics samples maintained their superhydrophobic properties even after 20 cycles, separation efficiency was still above 98.5 %. Our superhydrophobic cotton fabric demonstrated a remarkable separation of emulsified oil. We believe that our quick and environmentally friendly method can be used in variety of applications involving water-in-oil emulsion separation and oil purification.

Keywords: Superhydrophobic cotton fabric, Thiol-alkenes click reaction, Water-in-oil emulsion separation, De-emulsification

Introduction

Water pollution is a serious problem aggravated by recent economic developments and rapid population growth [1]. Contaminated waters especially containing insoluble oils and aromatic compounds as main pollutants, severely affects human health and ecosystems. Thus, a lot of efforts are undergoing to develop materials and approaches to efficiently decontaminate water. Such methods include but not limited to oil/water separation as well as adsorption and photocatalyzed decomposition techniques [2-4].

Newly developed superhydrophobic/superoleophilic materials, structure and working mechanism of which were inspired by lotus leaves, including particles, membranes and sponges, remove insoluble organic pollutants from water very efficiently because of their excellent oil/water selectivity [5-7]. Such superior performances attributed to the unique surface roughness of these structures as well as low surface energy and different surface tension of most oils and water. Oil-water separation occurs at the interface, thus intelligent strategies based on special wettability are very effective and advantageous [8,9].

Fabrication of superhydrophobic surfaces became very popular during recent years. For example, two-step processes include roughening the surfaces (as a first step) using nanoparticles (NPs), physical etching, lithography, template-assisted deposition, sputter coating, or sol-gel route. Second step involves low-surface energy treatment, Fluorine-containing hydrophobizing agents are considered among the most effective ones [10,11]. The best hydrophobic performance was obtained by applying fluoroorganosilicons which combine unique properties of both F and Si. Many different methods for preparing superhydrophobic materials were reported. One of the most common methods is fabrication of micro/nanostructures on the surface of different materials (metal, glass, ceramics, polymers, etc.) [12,13].

Wettability depends on the surface roughness and chemical composition Roughness can be obtained by imitating naturally rough surfaces (biomimetics). However, most of such surfaces could not be recreated during textile mass-production. However, recent progress and application of electrospinning, plasma treatment and sol-gel technology for nanomaterials provided breakthroughs allowing industrial production of superhydrophobic self-cleaning textiles. Boinovich *et al.* [14] prepared superhydrophobic aluminium alloy surface with water contact angle > 173 ° by laser ablation and low surface energy molecule modification Rather *et al.* [15] prepared superhydrophobic cotton by 1,4 conjugate addition reaction using polyethyleneimine, pentaerythritol and octadecylamine. Performance of this modified cotton fabric remained good even after repeated extrusion, ultraviolet irradiation and chemical radiation. Wang *et al.* [16] synthesized superhydrophobic coatings with polytetrafluoroethylene and fluorocarbon surfactants. These coatings could be applied to glass, cotton fabrics,

*Corresponding author: lzyongclin@sina.com
[†]These authors contribute equally to this work.

wood and other materials. However, fluorine-containing polymeric coatings are expensive and toxic. They also tend to bioaccumulate in flora and fauna, representing significant risks to human and ecosystem health.

In our previous work, Peng *et al.* [17] prepared an aerogel for oil/water separation consisting of superhydrophobic cellulose and chitosan composite (SCECS) using sol-gel method combined with freeze-drying. SCECS three-dimensional aerogel had high adsorption capacity and very porous structure, yet, it was not suitable for filtration and its separation efficiency was limited by the aperture. Wang *et al.* [18] designed pH-responsive material for oil-water separation using cotton fabric: this material was able to switch its hydrophilicity and hydrophobicity based on pH. However, all these modification were difficult and lengthy procedures and used fluorinated compounds.

Thus, in this work, to achieve effective and quick separation of highly stable water-in-oil emulsions, green and biodegradable cotton fabric was modified with SiO_2 to provide micro/nanoscale roughness. Thiol-ene click reaction between 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) and *n*-dodecyl mercaptan (NDM) resulted in a low-surface energy chemical modifier, which was consequently applied to the rough cotton fabric (see Scheme 1). Thio-ether bond was a strong covalent bond [19-23]. Because of long hydrophobic alkane chains and micro/nanoscale roughness, pure oil can freely pass through the superhydrophobic cotton fabric and be separated from water. Thus, demulsification and separation occurs when water/oil emulsion is dropped onto the cotton fabric: oil quickly permeates and passes through the superhydrophobic filter and long hydrophobic alkane chains. Water droplets remain aggregated on the surface of the cotton fabric because they are blocked by the hydrophobic alkanes. To test reusability of this superhydrophobic cotton fabric, 20 consecutive separation cycles were performed. Separation efficiency was assessed after each cycle. Our superhydrophobic cotton fabric demonstrated excellent superhydrophobicity, which make it an excellent material for continuous and simultaneous removal of insoluble and emulsified oil with high separation efficiency.

Experimental

Materials

Cotton fabric was purchased from a regular store. 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA), n-dodecyl mercaptan (NDM), 2,2'-Azobis(2-methylpropionitrile) (AIBN), tetraethyl orthosilicate (of analytical grade), ammonia solution (25-28 %), N,N-dimethylformamide (DMF) (of analytical grade) and ethanol (also of analytical grade) were purchased from Aladdin. All solutions were prepared using deionized (DI) water.

Preparation of SiO_2

Solution A:9 m*l* ammonia solution (25-28 %), 16.25 m*l* anhydrous ethanol, 24.75 m*l* water, were placed in a beaker, magnetic stirring (1000 r/min), Solution B:4.5 m*l* ethyl silicate, 45.5 m*l* ethanol, mixed evenly, was added to solution A to stir response 2 hours at room temperature, then centrifugal (10000 r/min) 10 min, ethanol washing 3 times,
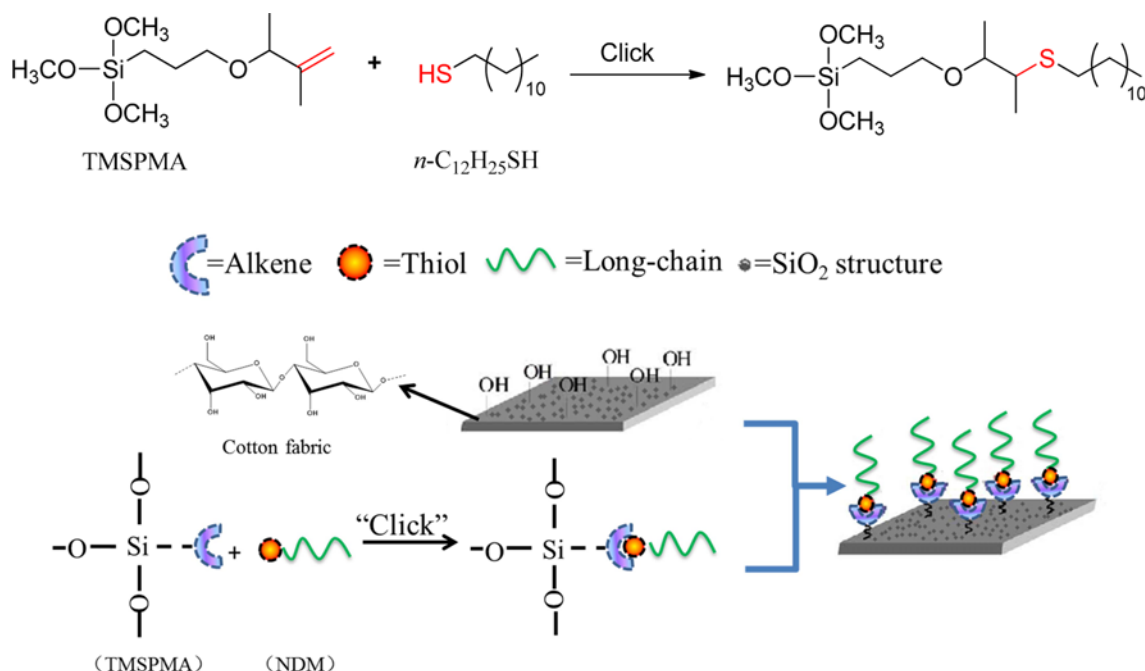
Scheme 1. Fabrication process of the hydrophobic cotton fabric.

50 °C of vacuum drying 2 h.

Preparation of Thiol-ene Hydrophobic Solution

Thiol-ene hydrophobic solution was prepared by simple binary polymerization. The TMSPMA (2.483 g, 10 mmol), NDM (2.024 g 10 mmol) were added to DMF (20 m*l*) in a 100 m*l* three-necked flask. And then, it was added to the initiator AIBN (0.676 g, 4.12 mmol) under nitrogen atmosphere in order to exhaust air in a reactionflask, magnetic stirring for 6 h at 60 °C. Then, dialysis 48 h with 300 Da dialysis bags. Finally, the copolymer solution is evaporated to remove water.

Preparation of Hydrophobic Cotton Fabric

Cotton fabric pretreatment: cotton fabric must be boiled in 2 % NaOH solution with 10 min and washed with distilled water in order to remove impurities and wax layers. 10 m*l* DMF, 0.5 g thiol-ene solution, 0.5 g SiO_2 were placed in a beaker, 5 cm×5 cm cotton fabric was dipped with 12 h by drying at 150 °C for 1 h. The whole process of hydrophobic cotton fabric preparation was showed in Scheme 1.

Characterization

FT-IR spectra of hydrophobic solution and hydrophobic cotton fabric were characterized using Nicolet Avatar 360 FT-IR spectrometer in the range of 4000-400 cm^{-1} in KBr pellets. The morphologies of hydrophobic cotton fabric were determined by scanning electron microscope (JSM-6490LV, Japan) with an accelerating voltage of 15 kV. The water contact angles are measured by a contact angle meter (DSA100, Kruss). 5 μl water was dropped onto the surface of the hydrophobic cotton fabric and five locations are tested in order to get the average value as final contact angle. A microscope (BX53, Olympus) was used to observe droplets in emulsions. The droplet sizes were confirmed by dynamic light scattering (DLS) measurements.

Results and Discussion

SEM micrographs demonstrated that surface of unmodified cotton fabric was smooth and had texture corresponding to the str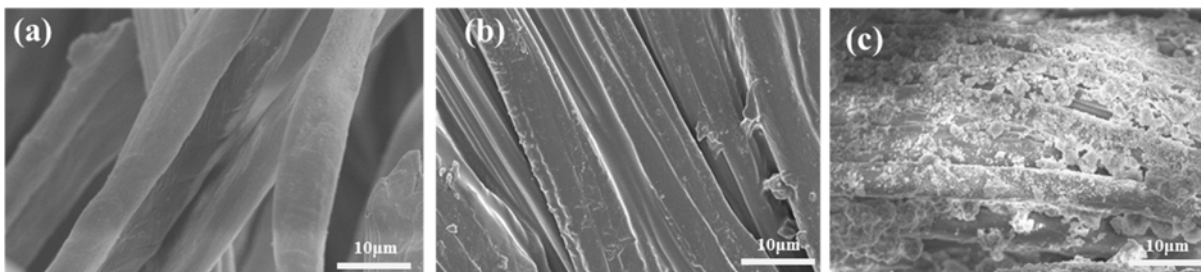eak fibers (see Figure 1(a)). Irregular flocs were observed on the modified cotton fabric (see Figure 1(b)). As SiO_2 content increased, surface roughness increased, and many micron-diameter particles were observed on the surface of the hydrophobic cotton (see Figure 1(c)).

The FTIR spectra of cotton fabric, modified cotton fabric were shown in Figure 2. It could be seen from the spectra of cotton fabric that several characteristic peak were located at 3348 cm^{-1}, 2890 cm^{-1}, 1430 cm^{-1}, 1050 cm^{-1} corresponding to -OH, C-H, -CH$_2$, C-O-C stretching band, respectively. But there were several new peaks in modified cotton fabric as 1733 cm^{-1}, 1281 cm^{-1}, 1060 cm^{-1}, 665 cm^{-1} corresponding to -C=O, -Si-C, -C-S-C, -Si-O-Si stretching band, respectively. The presence of these peaks proves that the thiol-ene hydrophobic segments are successfully grafted onto cotton fabric.

Cotton grafted with thiol-ene hydrophobic segments showed very stable superhydrophobicity. Wetting properties of unmodified and hydrophobic cotton fabric were characterized by water contact angle measurements (see Figure 3).

Figure 3(a) showed water droplets on unmodified cotton fabric. Water droplets completely immersed into the unmodified cotton within 15 s. Figure 3(b) shows that
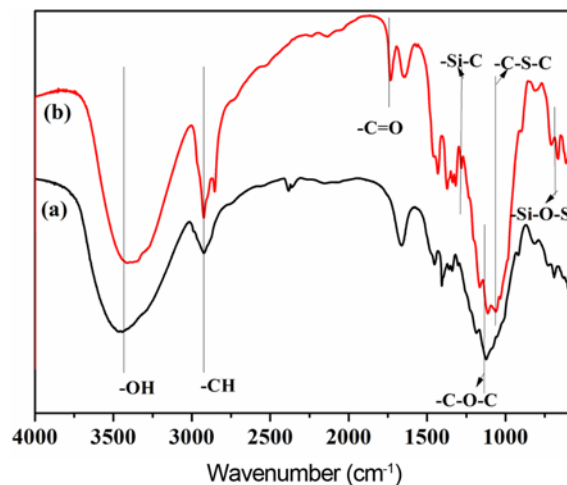

Figure 2. FTIR spectra of samples; (a) unmodified cotton fabric and (b) modified cotton fabric.

Figure 1. SEM images of sample; (a) unmodified cotton fabric, (b) polymer hydrophobic modified cotton fabric, and (c) superhydrophobic modified cotton fabric.
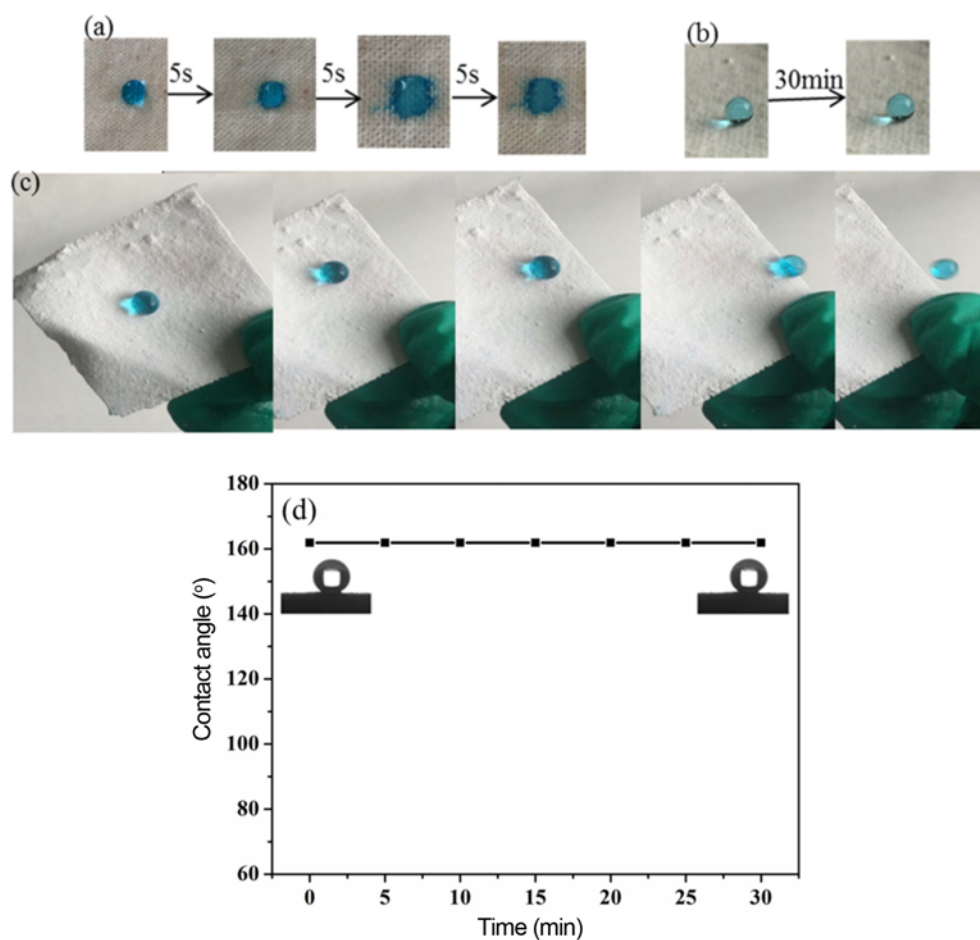
Figure 3. Wetting properties of the cotton fabric; (a) photographs of water fallen on the unmodified cotton fabric, (b) photographs of water fallen on the hydrophobic cotton fabric, (c) photographs of water rolled at random on the hydrophobic cotton fabric, and (d) contact angle of hydrophobic cotton fabric for water.

modified cotton fabric was superhydrophobic, water droplet on the surface (which were colored with a blue dye) were spherical, which is typical for superhydrophobic interactions. Water droplets sitting on the modified superhydrophobic cotton fabric could be rolled off the fabric randomly (see Figure 3(c)). Water contact angle was consistently equal to 161±2 ° (see Figure 3(d)). Thus, our modified cotton fabric showed good superhydrophobicity.

We used cyclohexane, toluene, 1,2-dichloroethane, trichloromethane respectively to detect the oil and water separation capacity of the material, the results were showed in Figure 4.

To study separation performance of our superhydrophobic fabric, we used heavy oils (such as 1,2-Dichloroethane and trichloromethane) as well as light oils (such as cyclohexane, toluene and benzene) as the model substances. We used 1:1 oil/water volume ratio. Density of heavy oil was higher than density of water (see Figure 4(a), the density of heavy oil was heavier than water, it could be sufficient contact with

the superhydrophobic cotton fabric to achieve a good separation effect. In about 10 s, the 20 m*l* of mixed solution could be completely separated and the separation time was very short. From Figure 4(b), Superhydrophobic cotton fabric could separate 20 m*l* of light oil/water mixed solution completely within 15 s, Separation time of light oil/water mixture was a little longer than separation of heavy oil and water because density of light oil was lower than water density. Additionally, separation platform should be at a certain angle for the most efficient separation. Interface contact between the light oil/water mixture and our superhydrophobic cotton was smaller; therefore separation time was longer comparing to that of heavy oil/water mixture.

To study separation performance of superhydrophobic cotton fabric, we studied oil/water separation flux as well as separation efficiency of superhydrophobic cotton (see results in Figure 5).

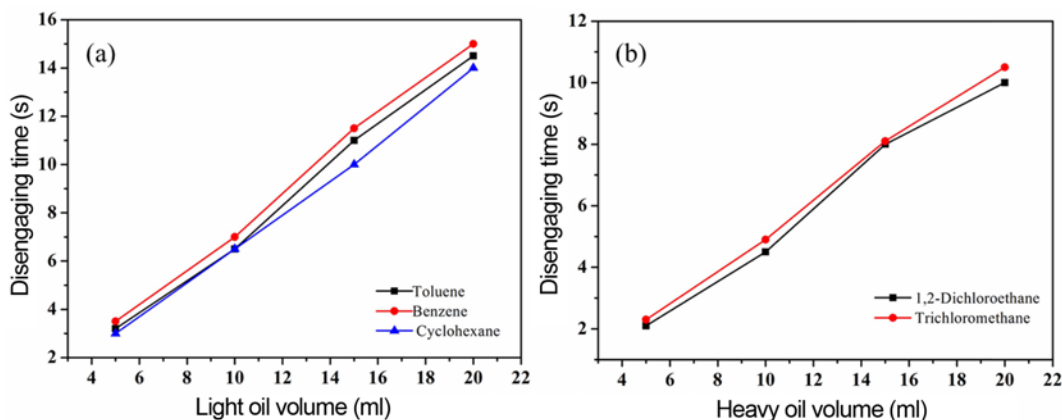The efficiency of oil-water separation was calculated

Figure 4. Oil and water separation of superhydrophobic cotton fabric; (a) separation of heavy oil from superhydrophobic cotton fabric and (b) separation of light oil from superhydrophobic cotton fabric.
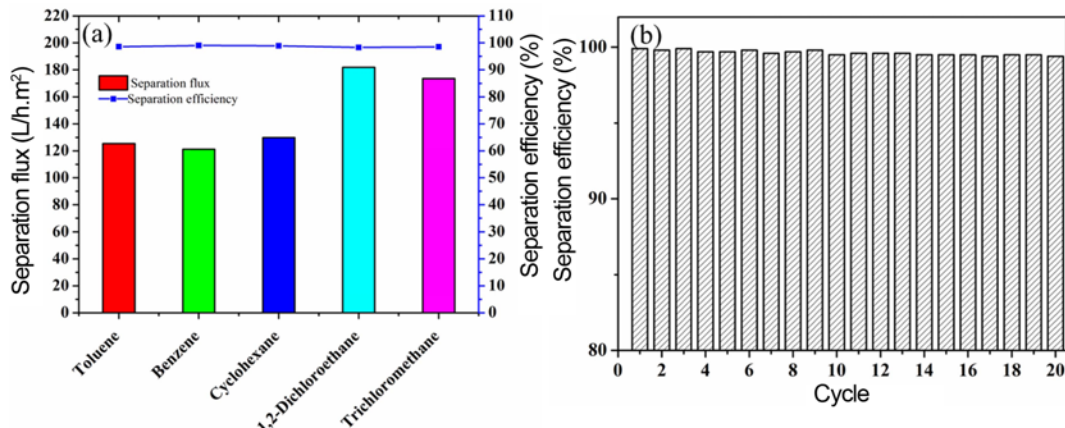

Figure 5. Oil and water separation performance of superhydrophobic cotton fabric; (a) separation flux and separation efficiency of superhydrophobic cotton fabric and (b) cyclic performance of superhydrophobic cotton fabric.

according to formula (1), and the separation flux was calculated according to formula (2) [24].

$$\eta = \frac{m_1}{m_0} \times 100\% \tag{1}$$

In the formula, η: separation efficiency (%)

m_1: solution after separation (g)

m_0: solution before separation (g)

$$J = V/(\theta \times A) \tag{2}$$

In the formula, J: flux (L/h·m^2)

θ: separation time (h)

A: separation area (m^2)

As shown in Figure 5(a), the experimental study on oil/water separation showed fine separability under normal pressure, the flux of the superhydrophobic fabric was above 120 L/(h·m^2) for the oil/water mixtures, the separation efficiency was up to 99 %. In Figure 5(b), after 20 cycles, the separation efficiency of the superhydrophobic cotton

fabric had almost no change, and it could still maintain the separation efficiency of more than 98.5 %. It showed that the performance of the material was superior.

The separation capacity of superhydrophobic cotton fabric for W/O emulsified oil was studied in the experiment, the stable emulsion was prepared by the 5 kinds of oil products. The oil and water were mixed with the ratio of 100:10 to the volume ratio. Then 0.2 % (wt%) surfactant Span-80, 1500 r/min was added at high speed to get the stable oil water type emulsion. As shown in Figure 6, the DLS particle size analysis was shown in Figure 7 (with toluene as the substrate).

As shown in Figure 6 (b), the separation consequence was examined by optical microscopy. From the left picture, it could be seen that the emulsion was the homogeneous milk white, the right image was filtered through the super-hydrophobic cotton fabric, which showed the demulsification was successful.

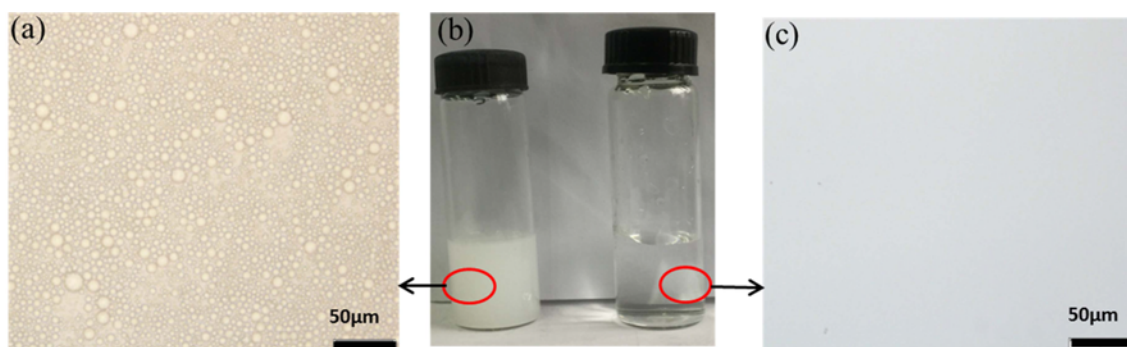As shown in Figure 6(a), the picture showed the picture of

Figure 6. Separation of emulsified oil from superhydrophobic cotton fabric; (a) optical microscope photo before separation of emulsified oil, (b) emulsified oil before and after separation (left) and after separation (right), and (c) optical microscope photo of emulsified oil after separation.
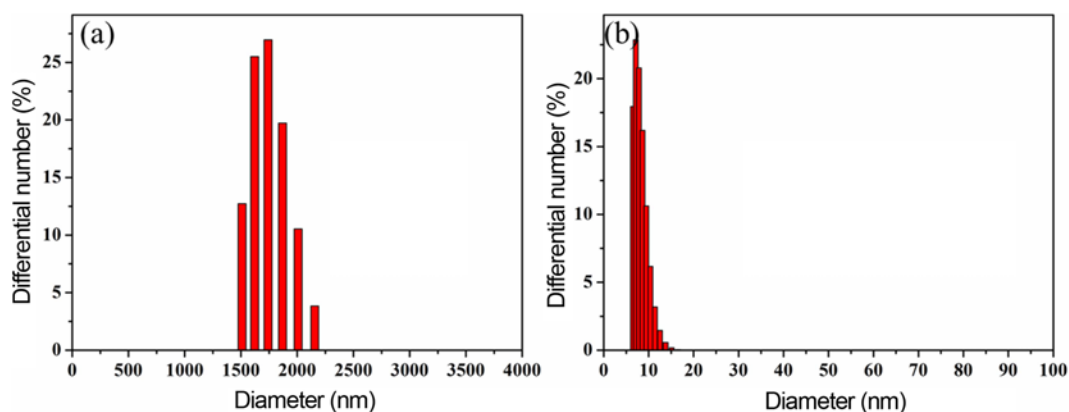

Figure 7. Particle size analysis of DLS before and after separation of emulsified oil with superhydrophobic cotton fabric; (a) DLS particle size analysis of emulsified oil before separation and (b) DLS size of filtrate after separation.

the emulsified oil was observed under the optical microscope. It could be seen from the picture that the emulsified oil particle size was uniform and the dispersing was better, the particle size was about 1 μm.

As shown in Figure 6(c), it was shown in the picture that the filtrate was observed under the optical microscope after the filtration and separation. The results show that the original feed was milky and possessed emulsion droplets, but the filtrate was transparent and no droplets were viewed by optical microscopy after filtrated. Thus, the superhydrophobic cotton fabric could be effectively retained in the emulsion to obtain pure oil.

As shown in Figure 7(a), the diameter of the emulsified oil before separation was about 1-2 μm. It was known from Figure 7(b) that the particle size of the filtrate after the separation of the superhydrophobic cotton fabric drops to about 10 nm, indicating that the superhydrophobic cotton fabric had a good separation ability.

To study separation performance of emulsified oil by our superhydrophobic cotton, we analyzed its separation flux and efficiency (see Figure 8).

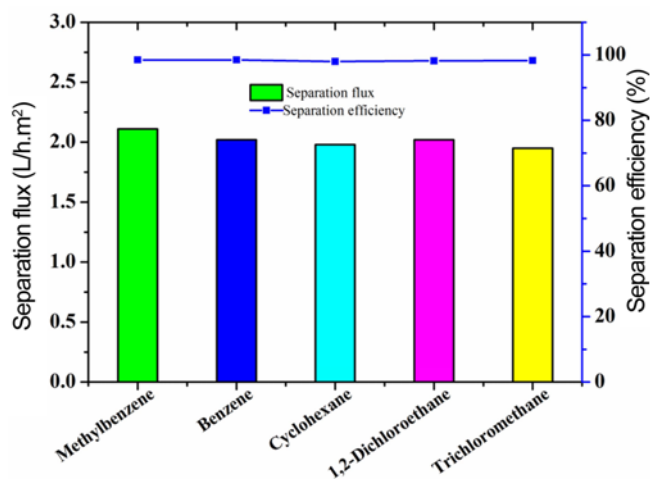Superhydrophobic cotton fabric again demonstrated good

Figure 8. Separation performance of superhydrophobic cotton fabric for emulsified oil.

separation efficiency (>98 %) in relationship to emulsified oil. Flux values for emulsified oils were also higher than those of regular oils.

Conclusion

In this paper, we had developed a simple strategy for fabricating superhydrophobic cotton fabric having the capacity to separate oil-water mixtures and surfactant-stabilized water-in-oil emulsions. Tt chemical composition, morphology, and hydrophobicity were studied by FTIR spectra, scanning electron microscopy (SEM), and water contact angle measurements, respectively. The flux of light oil and heavy oil all reach 120 L/(h·m^2), the separation efficiency could reach more than 99 %. After 20 cycles, the separation efficiency remained above 98.5 %. It was found that the diameter of the emulsified oil before separation was about 1 μm, and the filtrate particle size decreases to about 10 nm after separation, and the separation efficiency of the emulsified oil was above 98 %. Method of fabrication of superhydrophobic cotton fabric proposed in this work is simple, inexpensive and can be applied to other non-cotton fabrics to expand and promote fabrication of innovative textiles for wide variety of applications.

Acknowledgement

References

1. M. Zolfaghari, P. Drogui, and J. F. Blais, *Environ. Sci. Pollut. R.,* **25**, 7748 (2018).
2. H. Wang, H. Xu, W. Jia, and S. Ren, *J. Disper. Sci. Technol.,* **39**, 1 (2017).
3. Y. Li, M. Wang, D. Sun, Y. Li, and W. Tao, *Appl. Clay. Sci*., **2**, 1 (2018).
4. S. Huang, *ACS Appl. Mater. Inter.,* **6**, 17144 (2014).
5. R. H. Kollarigowda, S. Abraham, and C. D. Montemagno, *ACS Appl. Mater. Inter.,* **9**, 29812 (2017).
6. G. Meng, H. Peng, J. Wu, Y. Wang, W. Hao, Z. Liu, and X. Guo, *Fiber. Polym.,* **18**, 706 (2017).
7. Z. Wu, Y. Li, L. Zhang, Z. Yi, X. Hong, Z. Mao, B. Wang, and X. Sui, *Rsc Adv.,* **7**, 20147 (2017).
8. J. Gao, S. Xin, X. Huang, W. Ling, L. Bei, and H. Xue, *Appl. Surf. Sci.,* **439**, 394 (2018).
9. W. A. Khanday, F. Marrakchi, M. Asif, and B. H. Hameed, *J. Taiwan Inst. Chem. Eng.,* **70**, 32 (2016).
10. H. J. Ensikat, P. Ditsche-Kuru, and C. Neinhuis, *Beilstein J. Nanotech.,* **2**, 152 (2011).
11. Schutzius, M. Thomas, Bayer, S. Ilker, Tiwari, K. Manish, Megaridis, and M. Constantine, *Ind. Eng. Chem. Res.,* **50**, 11117 (2011).
12. C. Y. Chiu and Y. C. Lee, *J. Micromech. Microeng*., **19**, 105001 (2009).
13. L. Zhao, L. Lian, Y. Wang, J. Wu, G. Meng, Z. Liu, and X. Guo, *Appl. Phys. A-Mater.,* **124**, 9 (2018).
14. L. B. Boinovich, A. M. Emelyanenko, A. D. Modestov, A. G. Domantovsky, and K. A. Emelyanenko, *ACS Appl. Mater. Inter.,* **7**, 19500 (2015).
15. A. M. Rather, N. Jana, P. Hazarika, and U. Manna, *J. Mater. Chem. A.,* **5**, 1 (2017).
16. Z. Hua, H. Wang, H. Niu, Z. Yan, and L. Tong, *Adv. Funct. Mater.,* **27**, 1604261 (2017).
17. H. Peng, W. Hao, J. Wu, G. Meng, Y. Wang, Y. Shi, Z. Liu, and X. Guo, *Ind. Eng. Chem. Res.,* **55**, 1 (2016).
18. Q. Wang, G. Meng, J. Wu, Y. Wang, Z. Liu, and X. Guo, *Front. Mater. Sci.,* **12**, 1 (2018).
19. B. Yan and K. Qian, *Photochem. Photobiol.,* **85**, 1278 (2010).
20. G. Jin, D. Yu, Z. Guo, D. Yang, H. Zhang, A. Shen, J. Yan, and X. Liang, *Rsc Adv.,* **6**, 8584 (2016).
21. B. Liu, X. Deng, Z. Xie, Z. Cheng, P. Yang, and J. Lin, *Adv. Mater.,* **29**, 1604878 (2017).
22. W. Gang, J. Zhu, X. Chen, D. Hua, Q. Li, Z. Lei, and X. Cao, *Rsc Adv.,* **8**, 11036 (2018).
23. H. Liu, W. Zhu, and C. Sun, *Fiber. Polym.,* **19**, 580 (2018).
24. Q. Pan, W. Min, and H. Wang, *Appl. Surf. Sci.,* **254**, 6002 (2008).