Rational construction of highly transparent superhydrophobic coatings based on a non-particle, fluorine-free and water-rich system for versatile oil-water separation

Shouwei Gao,[a] Xiuli Dong,[a] Jianying Huang,[a] Shuhui Li,[a] Yuwei Li,[a] Zhong Chen,[b] and Yuekun Lai*,[a]

[a] National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, P. R. China.

[b] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore.

Corresponding Authors E-mail: yklai@suda.edu.cn

Abstract

Despite the existing effort, fabricating superhydrophobic substrate through an environmental friendly approach remains a great challenge. In the current work, we present a simple approach to fabricate robust superhydrophobic surfaces on different kinds of substrates using phase-separation method. This method uses (polydimethylsiloxane) PDMS as the binder, tetrahydrofuran (THF) as the solvent, and water as nonsolvent. The emulsion prepared under optimum proportion of THF and water was stable and showed no obvious change even after being stored for 6 weeks. The coated substrates exhibit superhydrophobic property with a water contact angle (CA) larger than 155.0°. Moreover, because the solution is rich of water, and the surface modification condition is mild, the PDMS coating enjoys a high degree of

transparency. Finally, superhydrophobic cotton and sponge were successfully demonstrated for oil-water and oil-in-water emulsion separation. This facile synthesis method has a potential for a broad range of applications in large-scale fabrication of superhydrophobic surfaces and filtration membranes.

Keyword: superhydrophobic, colored fabric, non-particle, fluorine-free, water-rich, oil-in-water emulsion separation

1. Introduction

Superhydrophobic surface with a water contact angle (CA) larger than 150º and a sliding angle (SA) lower than 10º has attracted enormous attention in a wide range of fields, including oil-water separation [1-3], drag-reduce devices [4-6], anti-icing coatings [7-8], and anti-wetting textiles [9-10]. A typical process to construct a superhydrophobic surface usually goes through two steps [11-14], for example, by first fabricating a micro-nano morphology, followed by modifying the surface with low surface energy materials. Numerous coating processes have been reported, including dip-coating [15-16], spray coating [17-18], plasma enhanced chemical vapor deposition [19-20], magnetron sputtering [21-22], and hot-pressing [23-24]. Among these, dip-coating of nanoparticles and curing of the binder is the most convenient and practical method to construct superhydrophobic surfaces without going through any time-consuming processes [25-26]. As an example, Lu et al. created a superhydrophobic surface by combining titanium dioxide (TiO_2) paint and adhesives. The coating showed a great resilience against various types of damages [27]. So far, most of studies in this field

relied on using nanoparticles to create the required micro-nano morphology, however, there is a potential concern over the toxicity of these particles once they are peeled off from the substrate during service [28]. Coupled with the relatively high cost of nanoparticle, it will be ideal if the surface rough features do not reply on use of nanoparticles. Another issue with conventional methods is the heavy use of organic solvents, such as ethanol and acetone, during coating preparation. These volatile solvents lead to safety concerns and will cause environment pollution [29]. Therefore, waterborne or water-rich coating systems are highly desirable [30].

Using water-rich self-roughening binder to fabricate superhydrophobic surface is able to resolve the above safety and environmental concerns. Polydimethylsiloxane (PDMS) is a common fluorine-free polymer binder used for fabricating superhydrophobic surfaces because of its outstanding water-repellency, high transparency, and excellent chemical stability [31-33]. Xue et al. reported a superhydrophobic poly(ethylene terephthalate) (PET) fabric via a nonsolvent-induced phase-separation method using PDMS based solutions as coating materials and ethanol as nonsolvent [34]. The use of ethanol in this case will cause harm to environment, and should be eliminated if possible.

Inspired by their works, we developed a fluorine-free and water-rich system without the addition of any particles to prepare superhydrophobic surfaces on different types of substrates. Through phase-separation, the coating system makes use of PDMS as the binder, tetrahydrofuran (THF) as the solvent, and water as non-solvent. The optimum proportion of THF and water was systematically explored.

Post-treated cotton fabric exhibited a great superhydrophobic property with CA and SA about 155.0° and 9.5° respectively without sacrificing the originally physical performance of the cotton. The surface also possessed excellent self-cleaning, anti-fouling, oil-water separation, and oil-in-water emulsion separation abilities. The prepared surface was also very stable under various physical and chemical conditions. Moreover, the use of transparent PDMS as well as the mild processing condition ensures no color change after the coating is applied. This overcomes the problem encountered by previous works in which the colored fabric was either etched or altered due to the presence of the nanoparticles [35-37]. This facile synthesis strategy has a broad implication in scalable fabrication of all kinds of superhydrophobic substrates.

2. Experimental work

2.1. Materials and reagents

Different kinds of fabrics including cotton (the diameter of individual cotton fibers is about 15 μm), silk, polyester, nylon, acrylic, viscose, ramie and wool fabrics were purchased from Shanghai Textile Industry. THF (analytical regent grade) and Hexadecane (analytical regent grade) were purchased from Chinasun Speciality Products Co., Ltd. PDMS (Dow Corning 184) was produced by Dow Corning Corporation. Colored fabric (61% cotton, 37% polyester, 2% spandex), patterned fabric and melamine sponge were obtained from local stores.

2.2. Preparation of dipping solution

PDMS, which contains pre-polymer and curing agent with the mass ratio of 10:1, was first dissolved in THF. Water was then dripped into the solution under ultrasonic shaking. The volume of the mixture solution was 100 ml in which the volume ratio of THF and water was varied from 10:0 to 1:9, and the concentration of PDMS was 1.0 wt%.

2.3. Fabricating superhydrophobic substrates

The substrates were soaked into the as-prepared solution for 30 min and subsequently baked at 120°C in a drying oven for 0.5 h.

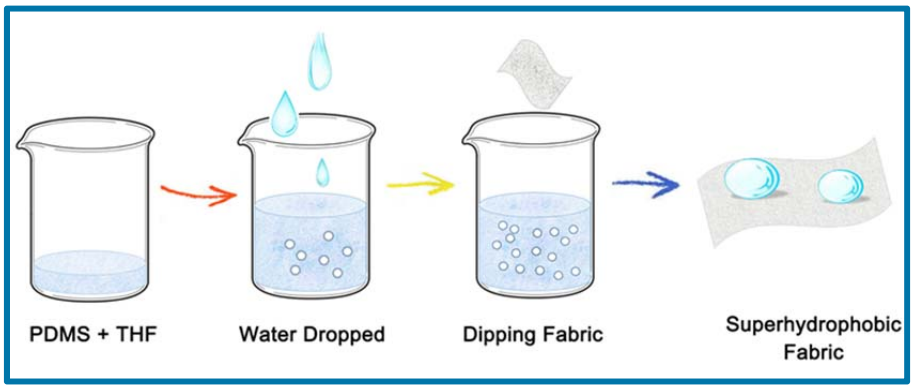
2.4. Preparation of oil-in-water emulsion

Surfactant-free oil-in-water emulsions were prepared by mixing toluene and water in a volume ratio of 1:99 and treated by 40 kHz ultrasonic stirring for 1 h. Surfactant-stabilized oil-in-water emulsions were prepared by mixing toluene and water in a volume ratio of 1:99 with addition of 0.1 g L^{-1} sodium dodecyl sulfate (SDS) and treated by 40 kHz ultrasonic stirring for 1 h.

2.5. Characterization

The microstructure was examined by a field emission scanning electron microscope (FESEM, Hitachi S-4800). Chemical composition was investigated by energy-dispersive X-ray spectrometer (EDS) and Kratos Axis-Ultra HAS X-ray photoelectron spectrometer (XPS). Fourier transform infrared (FTIR) spectroscopy was provided by (Nicolet 5700) instrument. Krüss DSA 100 (Krüss, Germany) apparatus was used to test the static and dynamic contact angle. Each sample was measured for 5 times at different places with 6 μl water or oil (hexadecane) droplet for

the static contact angle reading, and 15 μl for dynamic contact angle reading, respectively. The adhesive force between water and the coated surface was measured by a surface tension meter (Dataphysics DCAT11) at three different places. An atomic force microscope (AFM, Dimension Loon, Bruker) was used to measure the surface roughness, and each sample was tested for 3 times with the scanning area of 1 μm × 1 μm. The universal testing machine INSTRON-3365 was used to analyze the tensile strength and elongation at break of the fabrics. Moreover, air permeability, color, and flexural rigidity were characterized by a digital air permeability instrument (YG461E-11), spectrophotometric color measuring instrument (DATACOLOR 600), and fabric style instrument (KESFBAUTO-A), respectively. OLYMPUS BX51WI was employed for optical microscopy images.



Scheme 1. Schematic illustration of the procedures used to construct superhydrophobic fabric through a water-rich system.

3. Result and discussion

Scheme 1 shows the process to fabricate a superhydrophobic substrate. To explore an optimized condition, different volume ratios of THF and water from 10:0 to 1:9 were prepared. As shown in Fig. 1a, the transparency varied with different

solution conditions. Water contact measurement showed that the more turbid the solution was, the larger the CA on the modified cotton fabrics (Fig. 1b), when the volume ratio of THF and water was 10:0, the CA was smaller than 150°, which means the modified fabric wasn't superhydrophobic. With increasing water content, the CA increased. When the volume ratio of THF to water was 3:7, the as-prepared cotton fabric displayed the largest CA of 155.0 ± 0.6°. Further increasing water content leasds to a slight decrease in the CA. The droplet adhesive force was also measured to further understand the dynamic anti-wetting behaviour (Fig. S1, supplmental information). The results indicate consistent trend between the adhesive force and CA, i.e., samples with a higher CA has a lower droplet adhesive forces.

Although the chemical component is similar on various modified cotton fabrics, the wettability may also be affected by the surface topology of the PDMS coating. The representative surface roughness of the PDMS coated fiber was measured by AFM (Fig. 2a). It can be found that the root mean square (RMS) roughness value increased from 2.73 ± 0.17 nm to 13.90 ± 0.86 nm with the water volume ratio from 0 to 70%, followed by a slight decrease with the further increase of water content. The observation confirms that the surface roughness do have a great effect on the surface

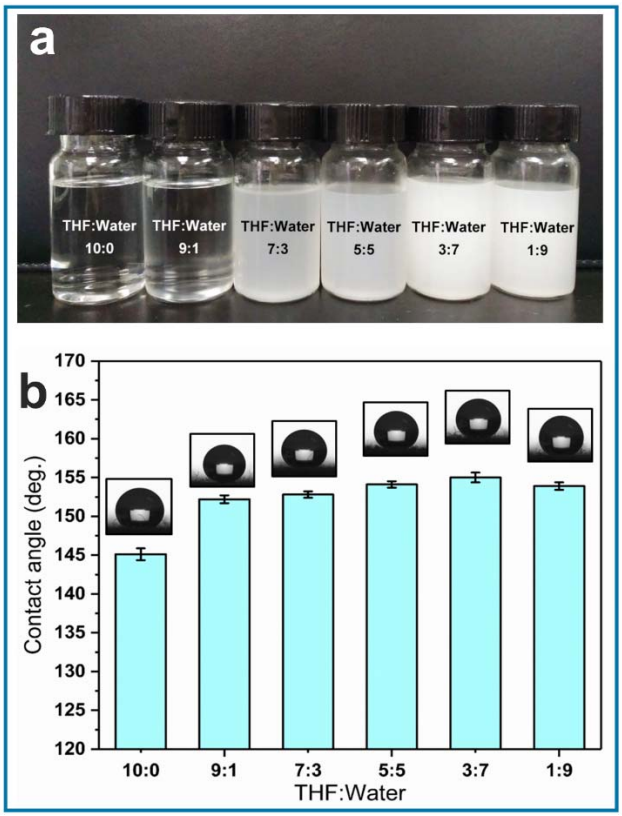


Figure 1. The picture of the dipping solution with different volume ratio for THF and water (a) and corresponding CA (b).

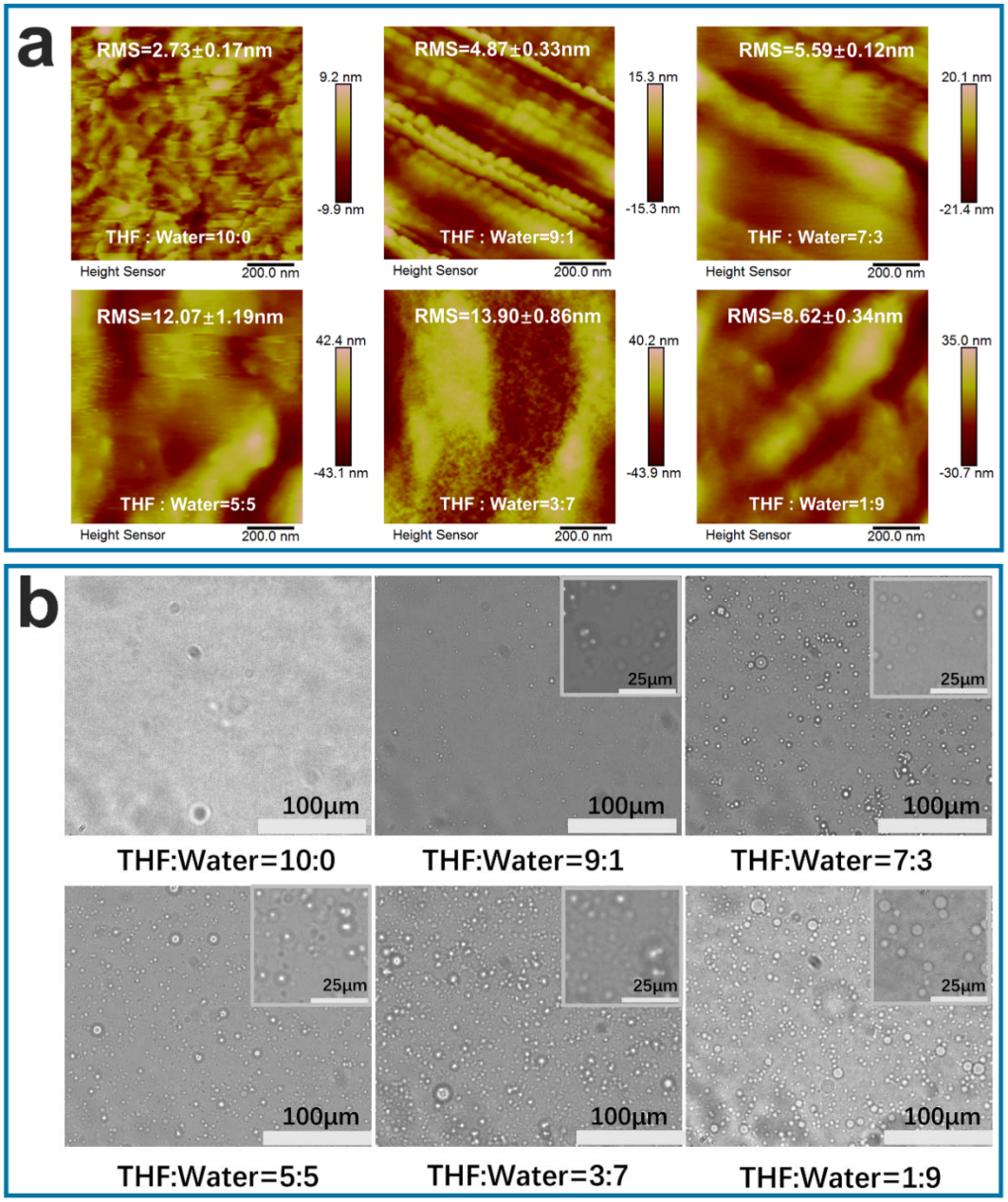
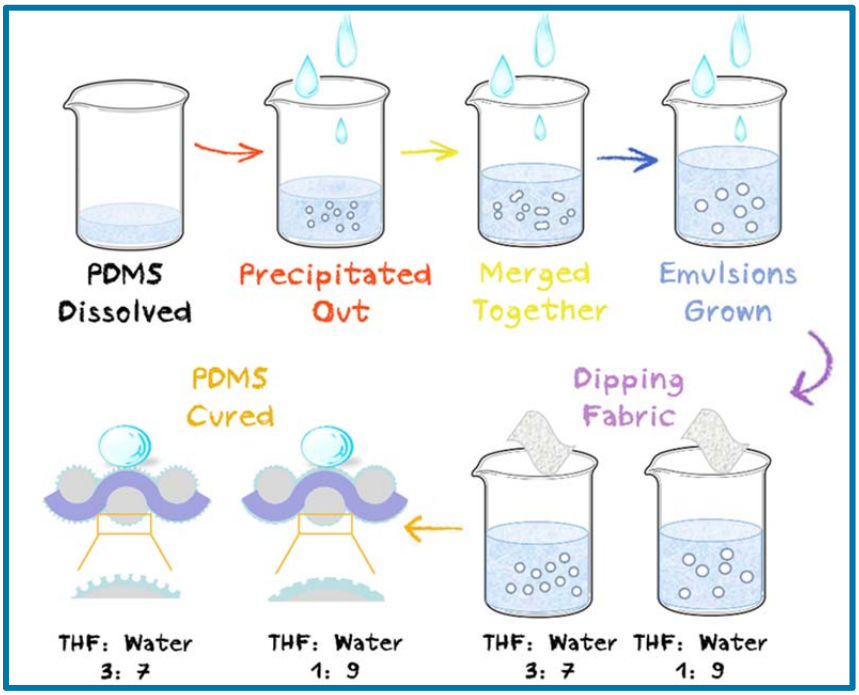


Figure 2. AFM roughness (a), and the optical microscopy images under different conditions (b).

It is of great interest to further understand why the ratio of solvent and non-solvent can effectively alter the surface roughness of the fiber and the resultant wettability of the fabric coating. Fig. 2b shows the optical microscopy images of the emulsion solution under different conditions. There was no emulsion when the solvent was THF only, while with the volume ratio of water increased, small emulsion droplets appeared and became larger in number and bigger in size as the water content

further increased. When the volume radio for THF to water was 3:7, the number reached a peak. At 1:9, the number of emulsions decreased, but the emulsion size was even larger. This behavior was similar to the precipitation process of organic compounds (Scheme 2). With more water added, the initial PDMS solution became over-saturated, so it precipitated out in the form of emulsion. The degree of super-saturation was different with different volume ratio of THF and the initial concentration of PDMS, which has contributed to the observed change of the number of emulsions. While as for the condition that the volume rado of THF to water was 1:9, coalescence occurred due to the high density of PDMS emulsion suspension, during which small emulsion droplets merged with its large neighbours leading to the increase in size but the decrease in number. As a result, in a THF-rich system, the PDMS spread around the fiber thus reduced the surface roughness (Fig. S2) because of the inherent mobility of un-cured polymer. As for a water-rich system, more but comparatively small emulsions contributed to a larger roughness because the time for curing was short. Since bulk emulsions take a longer time to cure, the emulsions have enough time to spread around the fiber that eventually decreased the roughness. In addition, it was worth noting that the as-prepared emulsion was quite stable. The solution can be stored for at least 6 weeks without observable change (Fig. S3).



Scheme 2. Schematic illustration of the mechanism for the different superhydrophobic property under different conditions.

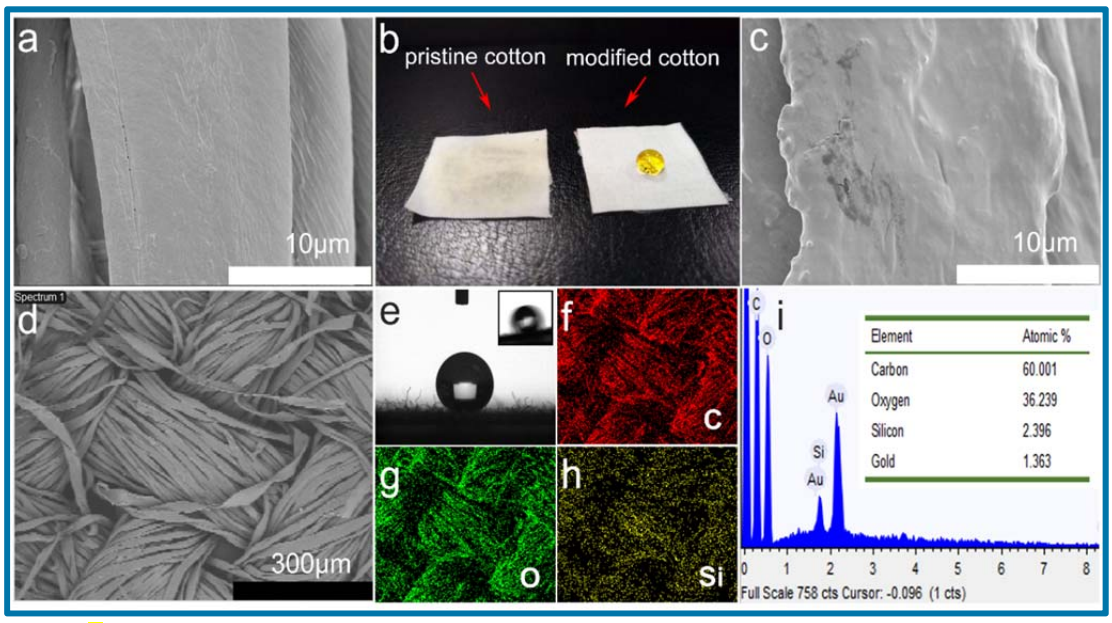


Figure 3. (a) the SEM image of pristine cotton fiber; (b) the photo of the droplets dyed by methyl orange on pristine cotton fabric and modified cotton fabric; (c, d) the SEM images of modified fiber with different enlargement factor; (e) the static behavior of droplet on the modified fabric, the insert was the corresponding dynamic behavior of droplet; (f - h) element mapping for C, O and Si; (i) EDS spectrum of the PDMS modified cotton.

A series of characterizations were introduced to test the properties of the coated surfaces. If not mentioned, the substrate was cotton fabric modified in dipping solution with the volume ratio of THF to water at 3:7. Fig. 3a and 3c, 3d are the SEM images of pristine cotton fiber and as-modified fiber. After the modification, EDS detected uniform silicon signal distribution on PDMS coated sampels (Fig. 3h and 3i), indicating a uniform PDMS coating on the cotton fibre surface (The Au element was caused by the thin gold nanoparticle sputter-coating on the fabric for SEM observation). The micro and nano morphology provided by the inherent fabric texture and after deposition of PDMS lead to a great superhydrophobic property with a CA and SA about 155.0 ± 0.6° and 9.5 ± 0.8°, respectively (Fig. 3b and 3e).

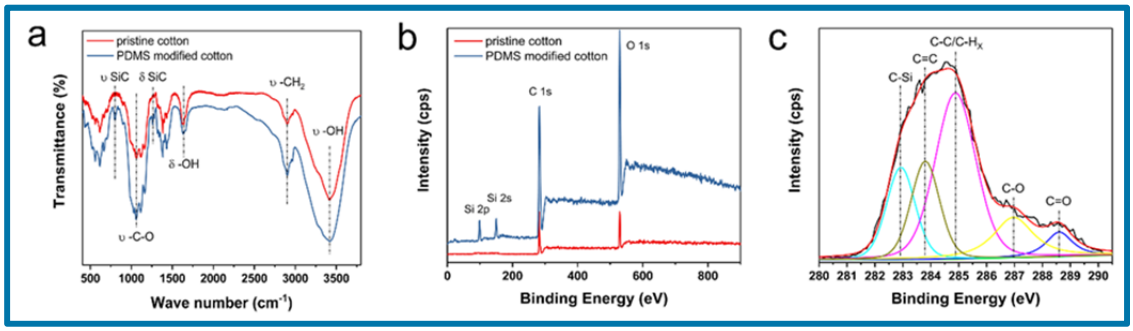


Figure 4. FTIR (a) and wide XPS (b) spectra of pristine and PDMS modified cottons; High resolution C 1s spectrum of modified cotton fabric (c).

FTIR and XPS were carried to further analyze the chemical composition. As shown in Fig. 4a, the absorption peaks at 3430 cm^{-1}, 2900 cm^{-1}, 1650 cm^{-1}, and 1160 - 980 cm^{-1} correspond to the stretching vibrations of -OH, stretching vibrations of -CH_2, bending vibrations of -OH and stretching vibrations of -C-O, respectively. After coated with PDMS, stretching vibrations and bending vibrations of Si-C appeared at 800 cm^{-1} and 1260 cm^{-1}, which indicates that the PDMS was successful modified on

the cotton. In addition, two new peaks appeared at 100.1 (Si 2p) and 150.5 eV (Si 2s) compared with the pristine cotton fabric, according to the XPS survey spectra (Fig. 4b, charge referenced by C-C at 284.9 eV). This also confirms the introduction of PDMS. Apart from these, as depicted in Fig. 4c, the high resolution C 1s peak exhibited five distinct peaks at 283.0 eV for C-Si bonds, 283.8 eV for C=C bonds, 284.9 eV for -CH_x (C-C and -CH_3) bonds, 286.9 eV for C-O-C bonds and 288.6 eV for C=O bonds, all of them are related to the coating of PDMS [38].

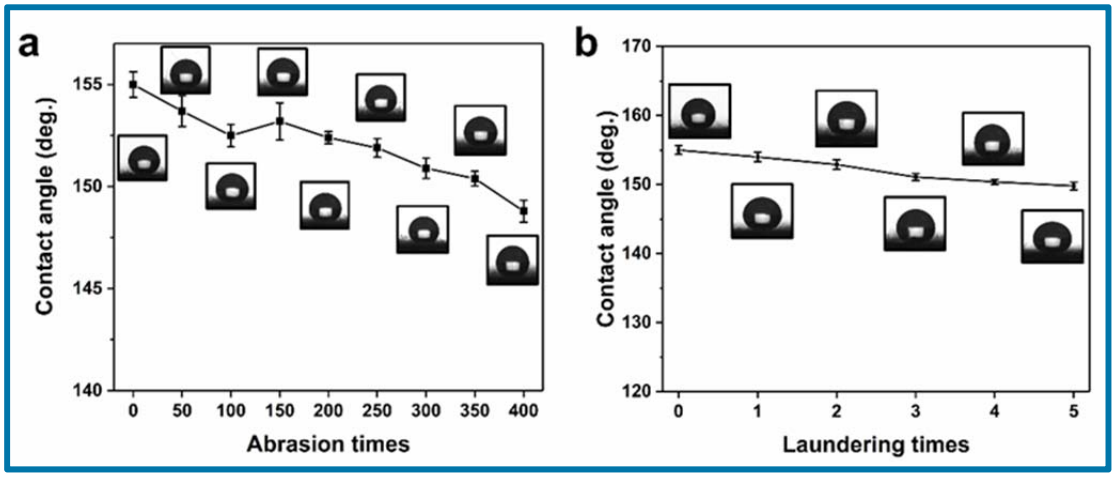


Figure 5. The effect of abrasion (a) and laundering (b) times on contact angle of the superhydrophobic cotton surface. The insets are the corresponding droplet images under different conditions.

Mechanical stability was assessed by taking the modified fabric under the pressure of 3.5 kPa with a pristine cotton fabric served as an abrasion surface. The abrasion test was carried out at a speed of 3 cm s^{-1} for a distance of 11 cm (defined as one abrasion cycle). As exhibited in Figure 5a, the CA decreased with increasing number of abrasion cycles, but still maintained around 150° after 400 cycles. Furthermore, accelerated laundering durability was calculated according to 2A

condition of the AATCC 61-2006 standard method. The modified cotton displayed no obvious CA decrease after 5 cycles (Fig. 5b). which indicates that as-modified fabric possessed a good durability during machine washing. In addition, to assess the ability against a high liquid pressure, PDMS modified cotton fabric was immersed into water. As displayed in Fig. 6a, a mirror-like surface was observed because of the entrapped air residing inside the fibers. On the contrast, the pristine cotton was saturated with water as soon as it was immersed because of its hydrophilic nature (Fig. 6b). Apart from these, the as-modified fabric can float on water, even when pressed down by the weight of a droplet sitting on its top (Fig. 6c). This suggests this type of coatings could be applied in shipbuilding industry [39].

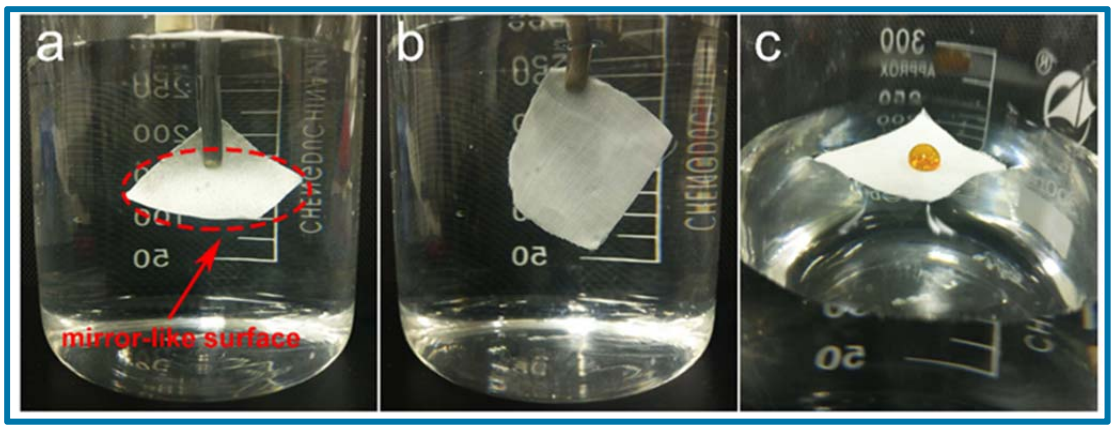


Figure 6. Images of the modified cotton (a) and pristine cotton (b) submerged in water; (c) as-modified cotton (2 cm × 2 cm) floated on the surface of water with a droplet (60 μl, dyed by methyl orange) on it.

Apart from the physical stability, chemical stability was also evaluated by immersing the as-prepared cotton into highly concentrated acidic solution (HCl, pH=1), salt solution (NaCl, pH=7) and basic solution (NaOH, pH=14) for 24 h. As

shown in Fig. 7, the as-modified fabric maintained superhydrophobic property even under such extreme chemical environments. The results can be explained by the superb chemical stability of PDMS that tightly wrapped around the fibers. The demonstrated stability would undoubtedly broaden its application in some extreme chemical conditions.

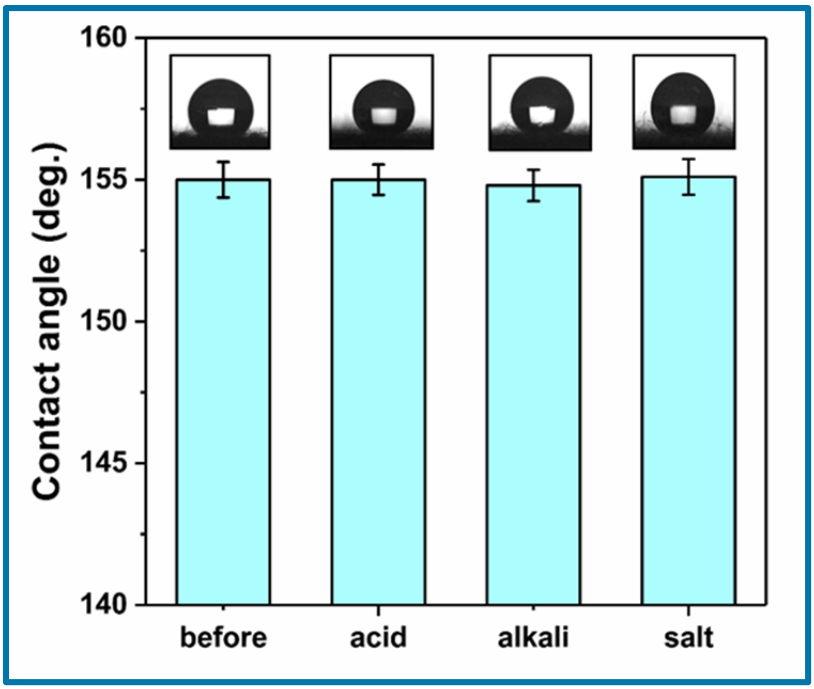


Figure 7. The contact angle of the droplet on modified fabric before and after immersed into HCl solution (pH=1), NaCl solution (pH=7) and NaOH solution (pH=14) for 24 h, Inset images are the corresponding droplets on the modified fabric.

Table 1. The physical properties of pristine cotton fabric and as-modified cotton fabric

Property	Pristine cotton	Modified cotton
Tensile strength (N cm^{-1})	468.95 ± 14.42 (warp)	426.48 ± 12.92 (warp)

	401.18 ± 15.05 (weft)	359.47 ± 20.39 (weft)
Elongation at break (%)	6.99 ± 0.23 (warp)	8.58 ± 0.24 (warp)
	19.35 ± 0.95 (weft)	26.22 ± 0.51 (weft)
	1244.1 (warp)	995.8 (warp)
Flexural rigidity (mg × mm)	400.0 (weft)	365.1 (weft)
	705.4 (total)	603.0 (total)
Air permeability (mm s^{-1})	430.4	281.8

It is to be noted the processing condition was generally mild, so that the physical properties such as tensile strength and flexural rigidity of the coated fabrics did not change much as shown in Table 1. Though the air permeability decreased from 430.4 to 281.8 mm s^{-1}, it was still larger than many other fabrics and it was good enough from the perspective of wear comfortability. The elongation at breakage has actually increased a lot owing to the outstanding elasticity of the PDMS. Beside the well maitained mechanical properties, the process did not impact heavily on the color of the substrates. To measure the color change, cotton-polyester blended fabric was chosen, because it was broadly used in the cloth industry. A color measuring instrument was employed to assess the influence of the coating on the color of the fabric. First, the UV-visible transmittance spectra was introduced to analyze the optical transparency of the PDMS coating in the range of 355-700 nm (Fig. 8a). The pristine fabric and the coated fabric displayed almost the same transmittance, proving that the PDMS coating is transparent. The images show that there was no obvious

change in color for the superhydrophobically modified fabric. To quantitatively characterize the change in color, the CIE L*, a*, and b* and ΔE* values were used, and the corresponding values are listed in Table 2. The result shows that the value of total color difference (ΔE*) was 1.21, which corresponds to a difference in color that is difficult to differentiate by naked eyes [40]. Different kinds of patterned fabrics were also employed as substrates (Fig. 8b), the patterns showed no change after modification. This means this method has a broad application potential for superhydrophobic modification for garment manufacturing.

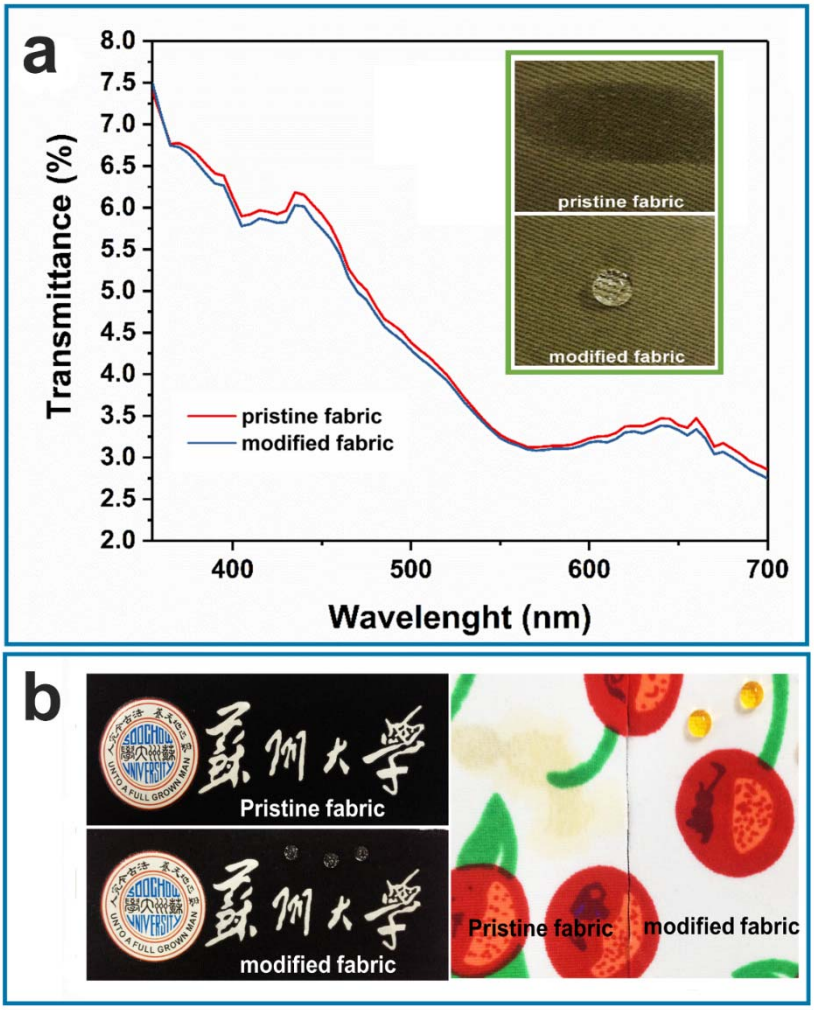


Figure 8. (a) The transmittance spectra of pristine colored fabric and the modified colored fabric. The insert are the imagines of pristine colored fabric and the modified colored fabric. (b) The

images of different kinds of patterned fabrics before and after modified. (Left: offset printing. Right: water printing)

Table 2. CIE L*, a*, and b* and ΔE* values for pristine colored fabric and modified fabric

	L*	a*	b*	ΔE*
Pristine colored fabric	40.75	-0.19	10.35	
Modified colored fabric	39.86	-0.362	11.158	1.21

This as-reported simple and practical superhydrophobic modification process is also suitable for different fabrics by commonly used natural or synthetic fibers, including silk, ramie, wool, viscose nylon, acrylic, and some hydrophobic fabric like polyester (Fig. 9a). It was noteworthy that all substrates displayed excellent superhydrophobic property. In addition, commercial melamine sponge was also employed as substrate. As shown in Fig. 9b, the sponge possessed a uniformly superhydrophobic property both outside and inside. This excellent anti-wetting effect was impossible to be realized by some other techniques such as spraying [41].

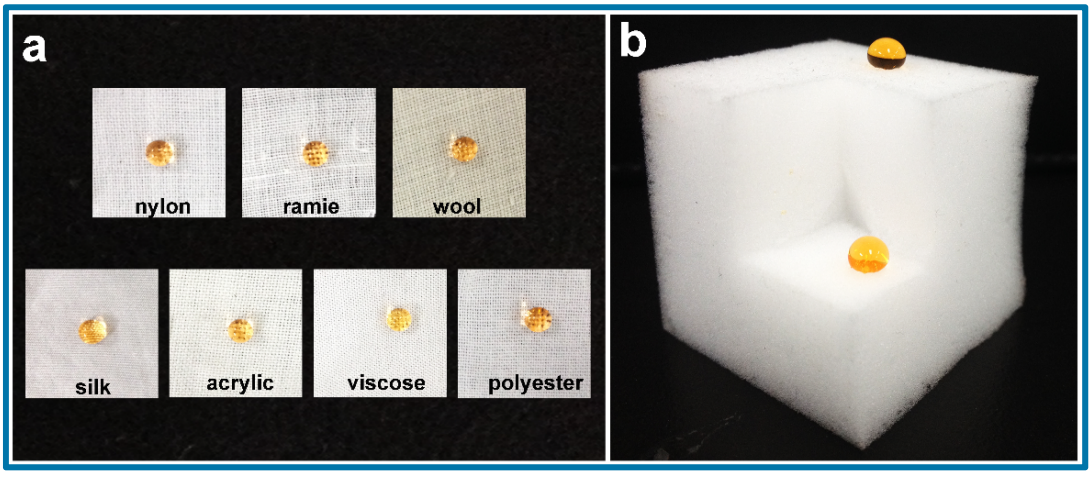


Figure 9. Different fabric substrates got superhydrophobic property after modification; (b)

commercial sponge obtained superhydrophobic ability on both inside and outside after modification.

Taking coffee powder as a model dust, the self-cleaning property was evaluated. As shown in Fig. 10a-c, the coffee powder was cast uniformly on both the pristine cotton fabric and the modified fabric. As water was dripped on to the fabric surface, the coffee powder on modified fabric was dissolved and taken away by the rolling water droplets leaving a clean surface behind. However, the white color of the pristine cotton was contaminated and dyed with the coffee powder that was dissolved in water.

Besides the self-cleaning performance, the superhydrophobic fabric also demonstrated excellent anti-fouling ability against dyes. It is seen in Fig. 10d-f that the pristine cotton was fully dyed by methylene blue solution (0.1 M) as soon as it was in contact with the solution, while for the modified fabric, no liquid was retained on its surface even after immersed deeply into the methylene blue solution.

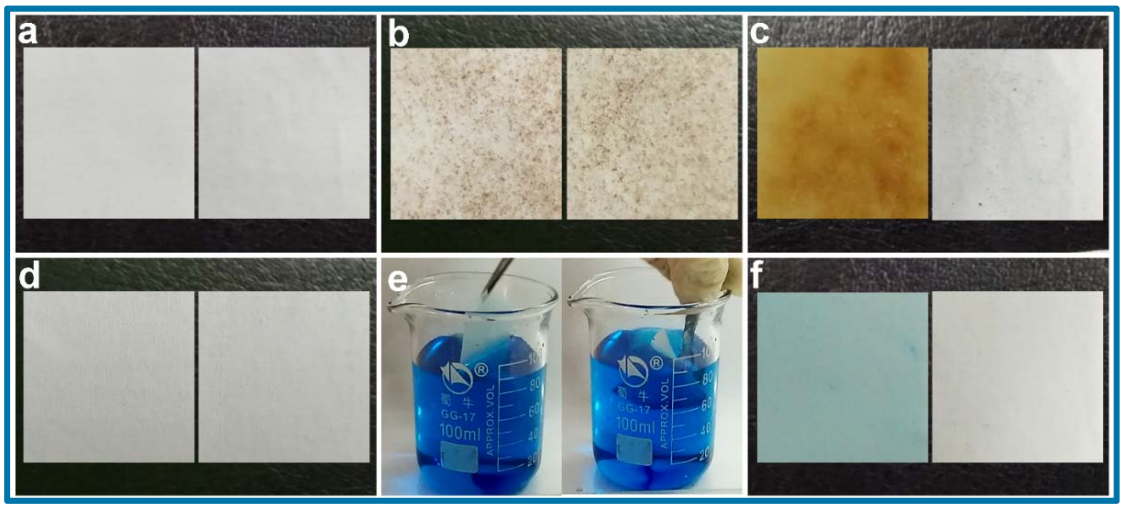


Figure 10. The self-cleaning process of the modified superhydrophobic fabric (a-c, the left was the pristine cotton, the right was the modified fabric); the anti-fouling property of different

samples (d-f): images of pristine cotton fabric (left) and modified cotton fabric (right) before (d) and after (f) be immersed into methylene blue solution and followed by being rinsed and dried.

The modified cotton fabric demonstrated superhydrophobic-superoleophilic properties (the CA of oil was shown in Fig. S4), so it was also used to demonstrate potential applications for oil-water separation. As shown in Fig. 11a-c, the superhydrophobic fabric was placed between two glass vessels. 100 ml oil (dichloromethane) and 100 ml water (dyed by methylene blue) were mixed and then poured onto the modified fabric membrane [42]. Because of the immiscibility of oil and water, the mixture was quickly layered (Fig. 11b) and the oil quickly permeated through the fabric, while the water was retained above the fabric due to the excellent superhydrophobic-superoleophilic ability for modified fabric (Fig. 11c). The separation efficiency was calculated based on the amount of collected product. The volume of the water was regarded as a reference because of its non-volatility. As shown in Fig. 11d, the volume of water after filtration was still 100 ml which means the separation efficiency for the modified fabric was ~100%. The same test was repeated 5 times with the same oil-water separation performance (Fig. S5).

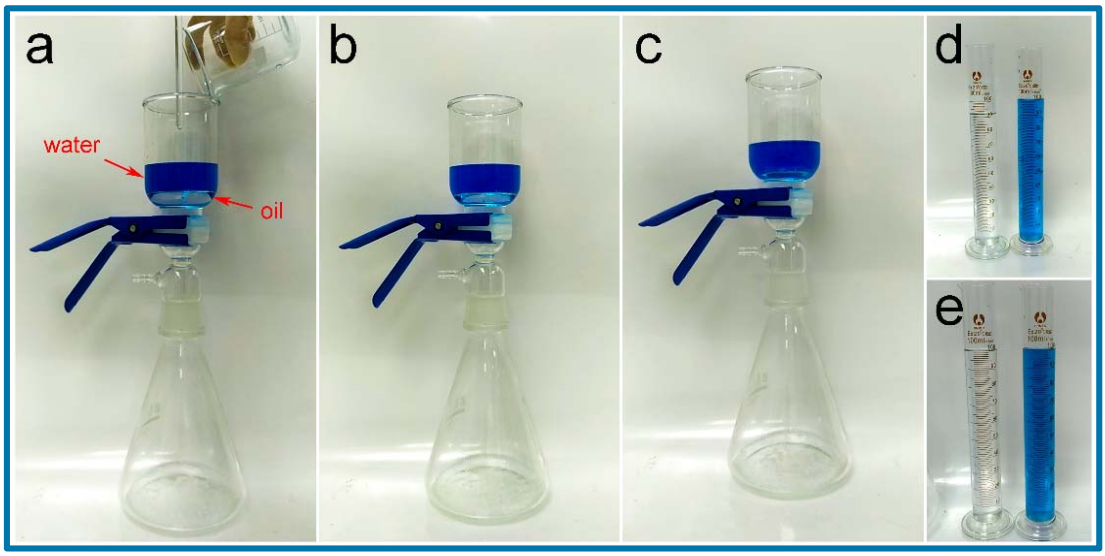


Figure 11. Time sequence of the oil-water separation process with modified fabric (a-c); the volume of water and dichloromethane before (d) and after (e) separation.

This superhydrophobic-superoleophilic sponge was chosen to separate oil-in-water emulsions. Both surfactant-free and surfactant-stabilized emulsions were prepared. The modified sponges were put into the emulsions and vigorously stirred. The emulsions gradually became transparent after most of the oil droplets were absorbed into the sponge [43]. Fig. 12 shows the imagines and micrographs of both surfactant-free and surfactant-stabilized emulsions before and after filtration by the superhydrophobic sponge. It could be seen that surfactant-free emulsion was turbid after ultrasonic treatment. The corresponding micrographs revealed that there existed plenty of emulsion droplets in the solution. While after separation, there was nearly no droplets left, implying the oil had been completely removed. Similar phenomenon was also found for the surfactant-stabilized system where the emulsion droplets were more stable. These results revealed the excellent separation performance for different kinds of oil-water mixtures through the modified 2D or 3D porous structures.

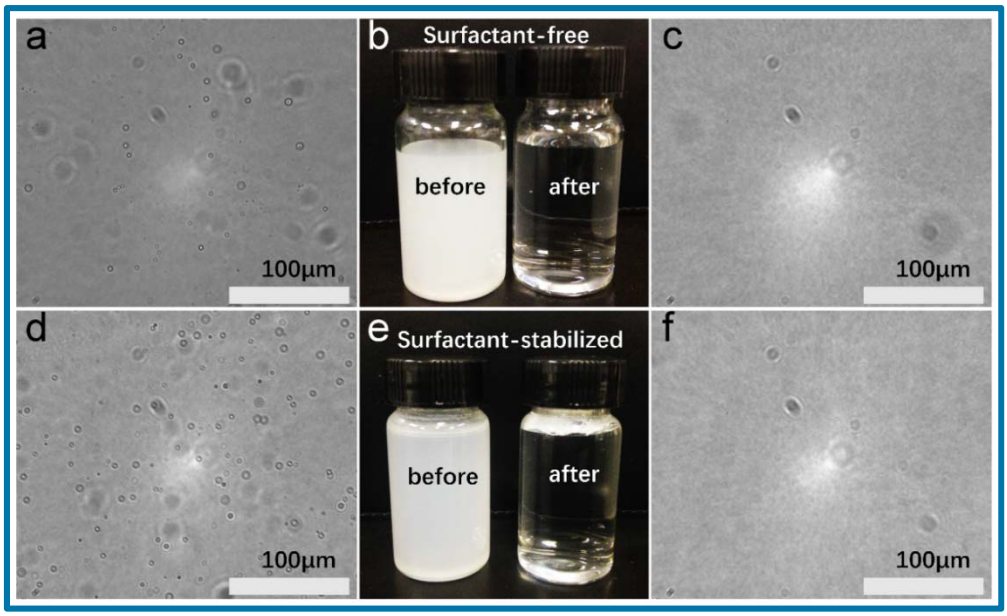


Figure 12. (a-c) The optical image and microscopic image of surfactant-free emulsions (b), before and after separation using modified sponge and corresponding micrographs (a, c); (d-f) The optical image of surfactant-stabilized emulsions (e), before and after separation using modified sponge and corresponding micrographs (d, f).

4. Conclusion

In summary, taking PDMS as the binder, tetrahydrofuran (THF) as solvent and water as nonsolvent, we introduced superhydrophobic property to different types of hydrophobic and hydrophilic substrates. The as-modified fabric showed an excellent superhydrophobic property with a CA larger than 150° and SA lower than 10° when the volume ratio of THF to water was 3:7. Such a fluorine-free and water-rich system does not require addition of nanoparticles. It does not affect the physical properties of the substrates or even has an increase for the elongation of the fabric. In addition, there is practically no change in the color of the fabrics. Through modifying a 2D fabric and 3D sponge, simple oil-water mixture and oil-water emulsions prepared by

both surfactant-free and surfactant-stabilized mehtods, can be respectively separated effectively. We propose that this facile synthesis method has a broad application potential for massive fabrication of different types of superhydrophobic substrates.

Acknowledgements

The authors acknowledge the National Natural Science Foundation of China (51502185; 21501127), Jiangsu Advanced Textile Engineering Center Project (Project No. SPPGO[2014]22), Nantong Science and Technology Project (GY12016030), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) for financial support of this work.

References

[1] L. Wang, Y. Zhao, Y. Tian, L. Jiang, A general strategy for the separation of immiscible organic liquids by manipulating the surface tensions of nanofibrous membranes, Angew. Chem. Int. Ed. 54 (2015) 14732-14737.

[2] X.J. Zeng, L. Qian, X.X. Yuan, C.L. Zhou, Z.W. Li, J. Cheng, S.P. Xu, S.F. Wang, P.H. Pi, X.F. Wen, Inspired by stenocara beetles: from water collection to high-efficiency water-in-oil emulsion separation. ACS Nano 11 (2017) 760-769.

[3] S.H. Li, J.Y. Huang, Z. Chen, G.Q. Chen, Y.K. Lai, A review on special wettability textiles: theoretical models, fabrication technologies and multifunctional applications. J. Mater. Chem. A 5 (2017) 31-55.

[4] I.U. Vakarelski, N.A. Patankar, J.O. Marston, D.Y.C. Chan, S.T. Thoroddsen, Stabilization of leidenfrost vapour layer by textured superhydrophobic surfaces. nature 489 (2012) 274-277.

[5] M.J. Cheng, M.M. Song, H.Y. Dong, F. Shi, Surface adhesive forces: a metric describing the drag-reducing effects of superhydrophobic coatings. Small 11 (2015) 1665-1671.

[6] D. Saranadhi, D.Y. Chen, J.A. Kleingartner, S. Srinivasan, R.E. Cohen, G.H. McKinley, Sustained drag reduction in a turbulent flow using a low-temperature leidenfrost surface. Science Adv. 2 (2016) E1600686.

[7] C.W. Lo, V. Sahoo, M.C. Lu, Control of ice formation. ACS Nano 11 (2017) 2665-2674.

[8] F.T. Liu, Q.M. Pan, Facile fabrication of robust ice-phobic polyurethane sponges. Adv. Mater. Interfaces 2 (2015) 1500219.

[9] S. Deng, J.Y. Huang, Z. Chen, Y.K. Lai, Controllable superhydrophobic coating on cotton fabric by UV induced thiol-ene reaction for wettability patterning and device metallization. Adv. Mater. Interfaces 4 (2017) 1700268.

[10] J.L. Sheng, Y. Xu, J.Y. Yu, B. Ding, Robust fluorine-free superhydrophobic amino-silicone oil/SiO_2 modification of electrospun polyacrylonitrile membranes for waterproof-breathable application. ACS Appl. Mater. Interfaces 9 (2017) 15139-15147.

[12] C.R. Szczepanski, T. Darmanin, F. Guittard, Spontaneous, Phase-Separation Induced Surface Roughness: A new method to design parahydrophobic polymer coatings with rose petal-like morphology repellent surfaces. turning a surface superrepellent even to completely wetting liquids. ACS Appl. Mater. Interfaces 8 (2016) 3063-3071.

[12] S. Alexander, J. Eastoe, A.M. Lord, F. Guittard, A.R. Barron, Branched hydrocarbon low surface energy materials for superhydrophobic nanoparticle derived surfaces. ACS Appl. Mater. Interfaces 8 (2016) 660-666.

[13] J.P. Zhang, S. Seeger, Superoleophobic coatings with ultralow sliding angles based on silicone nanofilaments. Angew. Chem. Int. Ed. 50 (2011) 6652-6656.

[14] S.N. Zhang, J.Y. Huang, Z. Chen, Y.K. Lai, Bioinspired special wettability surfaces: from fundamental research to water harvesting applications. Small 13 (2017) 1602992.

[15] X.Y. Zhang, Z. Li, K.S. Liu, L. Jiang, Bioinspired multifunctional foam with self-cleaning and oil/water separation. Adv. Funct. Mater. 23 (2013) 2881-2886.

[16] Z.G. Xu, Y. Zhao, H.X. Wang, X.G. Wang, T. Lin, A superamphiphobic coating withammonia-triggered transition to superhydrophilic and superoleophobic for oil-water separation. Angew. Chem. Int. Ed. 54 (2015) 4527-4530.

[17] D.F. Zhi, Y. Lu, S. Sathasivam, I.P. Parkin, X. Zhang, Large-scale fabrication of translucent and repairable superhydrophobic spray coatings with remarkable mechanical, chemical durability and UV resistance. J. Mater. Chem. A 5 (2017) 10622-10631.

[18] L.W. Chen, Z.G. Guo, W.M. Liu, Biomimetic multi-functional superamphiphobic FOTS-TiO_2 particles beyond lotus leaf. ACS Appl. Mater. Interfaces 8 (2016) 27188-27198.

[19] E. Gogolides, K. Ellinas, A. Tserepi, Hierarchical micro and nano structured, hydrophilic, superhydrophobic and superoleophobic surfaces incorporated in

microfluidics, microarrays and lab on chip microsystems. Microelectron. Eng. 132 (2015) 135-155.

[20] K. Ellinas, K. Tsougeni, P. S. Petrou, G. Boulousis, D. Tsoukleris, E. Pavlatou, A. Tserepi, S. E. Kakabakos, E. Gogolides, Three-dimensional plasma micro-nanotextured cyclo-olefin-polymer surfaces for biomolecule immobilization and environmentally stable superhydrophobic and superoleophobic behavior. Chem. Eng. J. 300 (2016) 394-403.

[21] F. Intranuovo, E. Sardella, P. Rossini, R. d'Agostino, P. Favia, PECVD of fluorocarbon coatings from hexafluoropropylene oxide: glow vs. afterglow. Chem. Vapor Depos. 15 (2009) 95-100.

[22] M. Petr, J. Hanus, O. Kylian, J. Kratochvil, P. Solar, D. Slavinska, H. Biederman, Superhydrophobic fluorine-free hierarchical coatings produced by vacuum based method. Mater. Lett. 167 (2016) 30-33.

[23] Y.F. Chen, S.Q Li, X.K. Pei, J.W. Zhou, X. Feng, S.H. Zhang, Y.Y. Cheng, H.W. Li, R.D. Han, B.A. Wang, Solvent-free hot-pressing method for preparing metal-oorganic-framework coatings. Angew. Chem. Int. Ed. 55 (2016) 3419-3423.

[24] S.W. Gao, J.Y. Huang, S.H. Li, H. Liu, F.Y. Li, Y.W. Li, G.Q. Chen, Y.K. Lai, Facile construction of robust fluorine-free superhydrophobic TiO_2@fabrics with excellent anti-fouling, water-oil separation and UV-protective properties. Mater. Des. 128 (2017) 1-8.

[25] P. Wang, M.J. Chen, H.L. Han, X.L. Fan, Q. Liu, J.F. Wang, Transparent and abrasion-resistant superhydrophobic coating with robust self-cleaning function in

either air or oil. J. Mater. Chem. A 4 (2016) 7869-7874.

[26] M.C. Wu, Y. Li, N. An, J.Q. Sun, Applied voltage and near-infrared light enable healing of superhydrophobicity loss caused by severe scratches in conductive superhydrophobic films. Adv. Funct. Mater. 26 (2016) 6777-6784.

[27] Y. Lu, S. Sathasivam, J.L. Song, C.R. Crick, C.J. Carmalt, I.P. Parkin, Robust self-cleaning surfaces that function when exposed to either air or oil. Science 347 (2015) 1132-1135.

[28] S.M. Hussain, L.K. Braydich-Stolle, A.M. Schrand, R.C. Murdock, K.O. Yu, D.M. Mattie, J.J. Schlager, M. Terrones, Toxicity evaluation for safe use of nanomaterials: recent achievements and technical challenges. Adv. Mater. 21 (2009) 1549-1559.

[29] H. Zhou, H.X. Wang, H.T. Niu, Y. Zhao, Z.G. Xu, T. Lin, A waterborne coating system for preparing robust, self-healing, superamphiphobic surfaces. Adv. Funct. Mater. (2017) 1604261.

[30] H. Ye, L.Q. Zhu, W.P. Li, H.C. Liu, H.N. Chen, Simple spray deposition of the water-based superhydrophobic coatings with high stability for flexible applications. J. Mater. Chem. A 5 (2017) 9882-9890.

[31] H. Liu, J.Y. Huang, Z. Chen, G.Q. Chen, K.Q. Zhang, S.S. Al-Deyab, Y.K. Lai, Robust translucent superhydrophobic PDMS/PMMA film by facile one-step spray for self-cleaning and efficient emulsion separation. Chem. Eng. J. 330 (2017) 26-35.

[32] T.X. Zhu, S.H. Li, J.Y. Huang, M. Mihailiasa, Y.K. Lai, Rational design of multi-layer superhydrophobic coating on cotton fabrics for UV shielding,

self-cleaning and oil-water separation, Mater. Des. 134 (2017) 342-351.

[33] C.Y. Cao, M.Z. Ge, J.Y. Huang, S.H. Li, S. Deng, S.N. Zhang, Z. Chen, K.Q. Zhang, S.S. Al-Deyab, Y.K. Lai, Robust fluorine-free superhydrophobic PDMS-ormosil@fabrics for highly effective self-cleaning and efficient oil-water separation. J. Mater. Chem. A 4 (2016) 12179-12187.

[34] C.H. Xue, Y.R. Li, J.L. Hou, L. Zhang, J.Z. Ma, S.T. Jia, Self-roughened superhydrophobic coatings for continuous oil–water separation. J. Mater. Chem. A 3 (2015) 10248-10253.

[35] Y.J. Zhang, J.P. Zhang, A.Q. Wang, From maya blue to biomimetic pigments: durable biomimetic pigments with self-cleaning property. J. Mater. Chem. A 4 (2016) 901-907.

[36] C.H. Xue, P. Zhang, J.Z. Ma, P.T. Ji, Y.R. Li, S.T. Jia, Long-lived superhydrophobic colorful surfaces. Chem. Commun. 49 (2013) 3588-3590.

[37] Z.Z. Gu, H. Uetsuka, K. Takahashi, R. Nakajima, H. Onishi, A. Fujishima, O. Sato, Structural color and the lotus effect. Angew. Chem. Int. Ed. 42 (2003) 894-897.

[38] X. Yang, Y. He, G.Y. Zeng, X. Chen, H. Shi, D.Y. Qing, F. Li, Q. Chen, Bio-inspired method for preparation of multiwall carbon nanotubes decorated superhydrophilic poly(vinylidene fluoride) membrane for oil/water emulsion separation. Chem. Eng. J. 321 (2017) 245-256.

[39] X.F. Gao, L. Jiang, Water-repellent legs of water striders. Nature 432 (2004) 36.

[40] M.E. Yazdanshenas, M. Shateri-Khalilabad, One-step synthesis of superhydrophobic coating on cotton fabric by ultrasound irradiation. Ind. Eng. Chem.

Res. 52 (2013) 12846-12854.

[41] D. Kim, H. Im, Y.K. Choi, J. Kwak Moo, G. Im Sung, E. Byun, A superamphiphobic sponge with mechanical durability and a self-cleaning effect. Sci. Rep. 6 (2016) 29993.

[42] S.H. Li, J.Y. Huang, M.Z. Ge, C.Y. Cao, S. Deng, S.N. Zhang, G.Q. Chen, K.Q. Zhang, S.S. Al-Deyab, Y.K. Lai, Robust flower-like TiO_2@cotton fabrics with special wettability for effective self-cleaning and versatile oil/water separation. Adv. Mater. Interfaces 2 (2015) 1500220.

[43] J.T. Wang, Y. Zheng, Oil/water mixtures and emulsions separation of stearic acid-functionalized sponge fabricated via a facile one-step coating method. Sep. Purif. Technol. 181 (2017) 183-191.

Supporting information

Rational construction of highly transparent Superhydrophobic coatings based on a non-particle, fluorine-free and water-rich system for versatile oil-water separation

Shouwei Gao,[a] Xiuli Dong,[a] Jianying Huang,[a] Shuhui Li,[a] Yuwei Li,[a] Zhong Chen,[b] and Yuekun Lai*,[a]

[a] National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, P. R. China.

[b] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore.

Corresponding Authors E-mail: yklai@suda.edu.cn

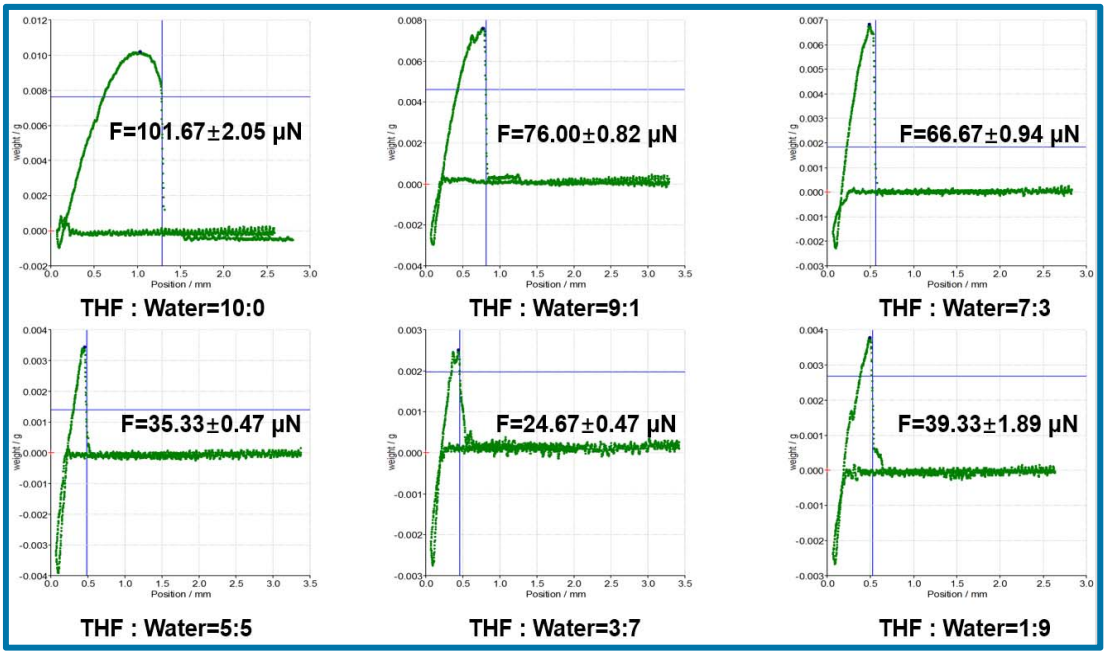


Figure S1. The adhesive force curves for the fabrics under different conditions.

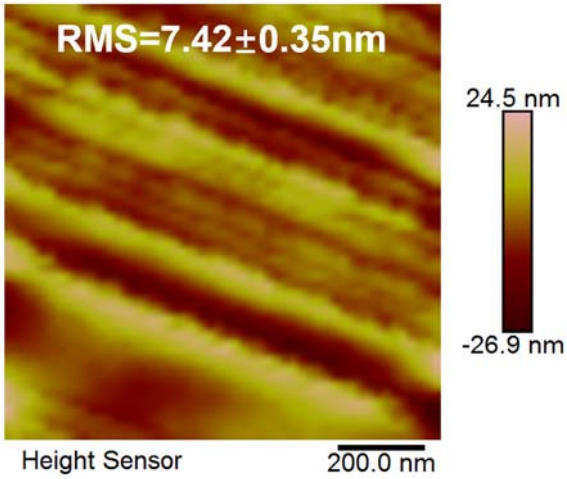


Figure S2. The AFM imagine of pristine cotton fabric.

Figure S3. The imagines of the dipping emulsion after stored for different period times with volume radio for THF and water was 3:7.

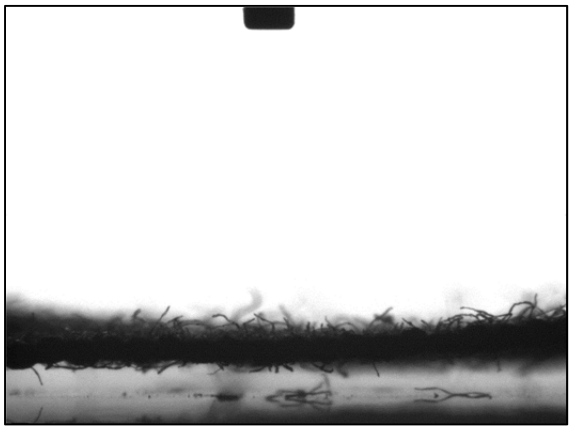


Figure S4. The imagines of the CA of oil for the fabric under the condition with volume radio for THF and water was 3:7.

Figure S5. The image of the volume of blue dyed water after 5 times continuous oil-water separation test.