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## Robust Superhydrophobic Surfaces by Modification of Chemically Roughened Fibers via Thiol-Ene Click Chemistry

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Superhydrophobic fabrics were fabricated by creation of roughening structures through alkali etching of fibers, modification with mercapto silanes and hydrophobization via thiol-ene click chemistry. Alkali etching resulted in nanoscale pits on the fiber surfaces roughening the fabrics with hierarchical structures, and improved the affinity of fibers for mercapto silanes. Click reaction between dodecafluoroheptyl methacrylate and sulfhydryl fibers lowered the surface energy, making the fabrics superhydrophobic with superoleophilicity. The as-obtained superhydrophobic fabrics showed excellent chemical robustness even after exposure to different chemicals, such as acid, base, salt, acetone, and toluene. Importantly, the fabrics maintained superhydrophobicity after 4500 abrasion cycles, 200 laundering cycles, as well as long time exposure to UV irradiation. The fabrics could be applied in oil/water separation due to the superhydrophobic and superoleophilic properties.

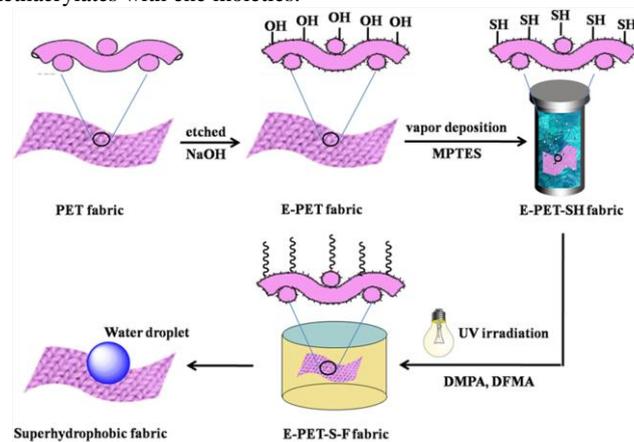
### Introduction

The fabrication of superhydrophobic surfaces is a fast growing area in both the scientific community as well as the industrial world due to their unique water-repellent and self-cleaning properties.<sup>1-12</sup> Their emerging applications include oil-water separation,<sup>13-17</sup> anti-icing,<sup>18</sup> protection of electronic devices,<sup>19</sup> and avoiding fluid drag in microfluidic devices.<sup>20</sup> It is well known that a superhydrophobic surface generally has a low surface energy material combined with a particular micro/nano structural roughness.<sup>21-25</sup> Using this principle, numerous artificial superhydrophobic surfaces have been prepared on different substrates adopting various methods/techniques.<sup>26-32</sup> Among these artificial superhydrophobic surfaces, water-repellent fabric is considered to be the most promising one.

Despite the significant progress made in developing superhydrophobic fabrics, it is still a great challenge to sustain the superhydrophobicity through laundering and abrasion during applications. Strategies that have been developed to improve the mechanical stability of surface superhydrophobicity include cross-linking the coating layer,<sup>33</sup> creating multiscaled roughness on the substrate,<sup>34-35</sup> introducing a bioinspired self-healing function,<sup>36-38</sup> endowing the coating with an elastomeric nanocomposite structure,<sup>39</sup> or establishing chemical bonds between the coating and substrate.<sup>3, 40-41</sup> Forming covalent bonds between fibers and low surface energy compounds is a critical point to enhance the stability of

superhydrophobic fabrics.

As a surface chemical modification platform, click reactions have been successfully applied to functionalize inorganic/organic substrates such as gold, graphene, silicon, collagen, and cellulose nanocrystal.<sup>42-48</sup> The great success of click chemistry lies in the mild reaction conditions needed, its high chemoselectivity, and the quantitative yields achieved.<sup>49-50</sup> Compared with traditional click chemistry, photoinitiated thiol-ene click chemistry has recently emerged as an elegant and appealing coupling reaction.<sup>51-52</sup> Very mild reaction conditions, the absence of a metal catalyst, and the ready availability of thiol-functionalized molecules are distinctive features of this coupling chemistry.<sup>52-58</sup> Enes can be chemically cross-linked onto substrates utilizing thiol-terminated surfaces, which are formed by the use of thiol silanes reacted with surface hydroxyl groups. Therefore, photoinitiated thiol-ene click chemistry should be a way to hydrophobize surfaces using hydrophobic methacrylates with ene moieties.



**Figure 1.** Illustration of the fabrication of superhydrophobic fabrics.

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In this work, we report the fabrication of superhydrophobic poly(ethylene terephthalate) (PET) fabrics by creation of roughening structures through alkali etching of fibers, modification with 3-mercaptopropyltriethoxysilane (MPTES) and hydrophobization with dodecafluoroheptyl methacrylate (DFMA) via thiol-ene click chemistry, as shown in Figure 1. The wettability tests showed that the superhydrophobic fabrics were robust to different chemicals and maintained superhydrophobicity after severe abrasion, laundering, as well as long time exposure to UV irradiation. And the superhydrophobic fabrics showed excellent oil/water separation performance.

## Experimental section

### Materials

PET fabric was purchased from a local factory. MPTES and 2,2-Dimethoxy-2-phenylacetophenone (DMPA) were purchased from Aladdin. DFMA was purchased from Harbin Xeogia Fluorine-silicon Material Co., Ltd. (China). Sodium hydroxide was purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. All chemicals were used as received.

### Chemical Etching of PET Fabrics

Chemical etching of PET fabrics was conducted through a modified procedure reported in our previous work.<sup>34, 35</sup> The original fabrics (25 cm×35 cm, 22±0.6 g) were cleaned with deionized water at 80°C for 30 min to remove the impurities and dried at 80°C for 10 min. The cleaned fabrics were dipped into 380 g/L sodium hydroxide solution for 5 min. Then the soaked fabrics were double-side covered in a polyethylene film and heated at 110°C for 3 min. Finally, the fabrics were rinsed with abundant water until the pH of the fabric surfaces reached 7 and dried at 80°C in an oven. Thus, chemically etched PET fabrics were obtained, denoted as E-PET.

### Mercapto Silane Modification of the Etched PET Fabrics

Chemical vapor deposition was used to form mercapto silane monolayer on the E-PET fabrics. Firstly, the E-PET fabrics were placed into a container with 0.1 mL MPTES added. Then the container was sealed and mounted in an infrared-rays heating machine, followed by heating according to a heating program to 90°C and held for 1.5 h.<sup>34, 41</sup> Finally, the samples were taken out, washed successively with anhydrous ethanol and deionized water, then dried at 80°C to obtain mercapto silane modified fabrics, denoted as E-PET-SH.

### Hydrophobization of Fabrics via Thiol-Ene Click Chemistry

Fabrics were immersed in a conical flask added with DMF (150 mL), DFMA (12 g, 30 mmol), and DMPA (0.03 g, 0.12 mmol). Then the conical flask was sealed and irradiated with UV light with an intensity of 300 W/m<sup>2</sup> at 370 nm from the top side for a given time. After the reaction, the samples were washed with anhydrous ethanol and deionized water. The resultant fabrics were dried at 80°C and denoted as E-PET-S-F.

### Characterization

The surface morphology of the fiber was examined using a Hitachi S-4800 field emission scanning electron microscope (SEM). Elemental analysis of the fiber surface was conducted by using K-alpha thermo Fisher Scientific X-ray photoelectron spectra (XPS). Contact angles (CAs) and sliding angles (SAs) were measured at 25°C with deionized water of 5 µL using a video optical contact angle system (OCA 20, Data physics, Germany). The reported values of CA and SA were determined by averaging values measured at six different points on each sample.

### Stability Evaluation of Superhydrophobic PET Fabrics

Aqueous solutions of different pH values and various organic solvents were used to test the chemical stability of superhydrophobic PET Fabrics. The modified fabric was soaked in the selected solutions or solvents for 72 h and dried at 80°C for CA measurement.

The abrasion tests were carried out according to a modified procedure based on the AATCCA Test Method 8-2001. Using a pure nylon fabric cloth as the abrasion partner, the sample was fixed onto the stainless steel column and moved repeatedly with a load pressure of 45 kPa (200 mm moving path for one cycle).

Laundry tests were performed by a laundry machine (SW-12 E, Fang Yuan, China) at 40°C in the presence of 10 stainless steel balls and 0.37 wt% soap powder in the washing containers. One washing cycle (45 min) is approximate to five times of commercial laundering. The washed fabrics were rinsed by abundant water to remove the residual detergent and dried at 80°C.

UV resistance was tested by irradiation using an artificial light source (UV lamp, Osram Ultra Vitalux 300 W) emitting a Gaussian-shaped spectrum which peaked at 370 nm with a cut off at 290 nm. Fabrics were placed under the UV lamp for continuous irradiation.

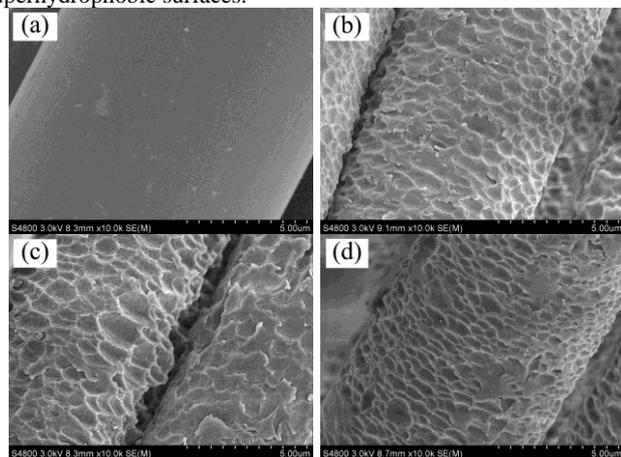
## Results and discussion

### Characterization of the Thiol-Ene Click Chemistry Modified Fabrics

In this study, superhydrophobic fabrics were fabricated by combining chemical etching of PET fibers with thiol-ene click chemistry. Firstly, PET fabrics were treated with sodium hydroxide to produce hydroxyl groups at the fiber surface due to the breaking down of ester groups of PET polymers. Meanwhile, finer structures could be induced on the fiber surface enhancing the roughness of fabric surfaces. The pits formed on the fiber surface were recognized to be caused at locations identified to be of lower crystallinity. The corresponding weight reduction and surface morphology of the fibers could be adjusted by the concentration and temperature of sodium hydroxide solution as well as the treatment method.<sup>34</sup> Secondly, reactions of mercapto silanes with hydroxyl groups at the fiber surfaces led to the formation of reactive thiol layers. Finally, the targeted superhydrophobic fabrics were subsequently prepared through the thiol-ene click chemistry using hydrophobic methacrylates with ene moieties.

The surface morphology of the original and the modified fabric were characterized by SEM. It was found that the fibers of the pristine PET fabrics were smooth with average diameter of about 11.5 µm (Figure 2a). However, after treatment with sodium

hydroxide, pits were formed on the fibers with diameter reduced to about 8.5  $\mu\text{m}$  and the fiber surface became extremely rough, as shown in Figure 2(b). Figure 2(c) shows that modification with mercapto silane did not cause obviously changes in the roughening morphology of the etched fibers. Also importantly, the surface morphology of E-PET-S-F fabrics was similar to that of E-PET and E-PET-SH, as shown in Figure 2(d). Maintaining of the fiber morphology helps to complement the microscale roughness inherent in the textile weave, directing to proper roughness for superhydrophobic surfaces.



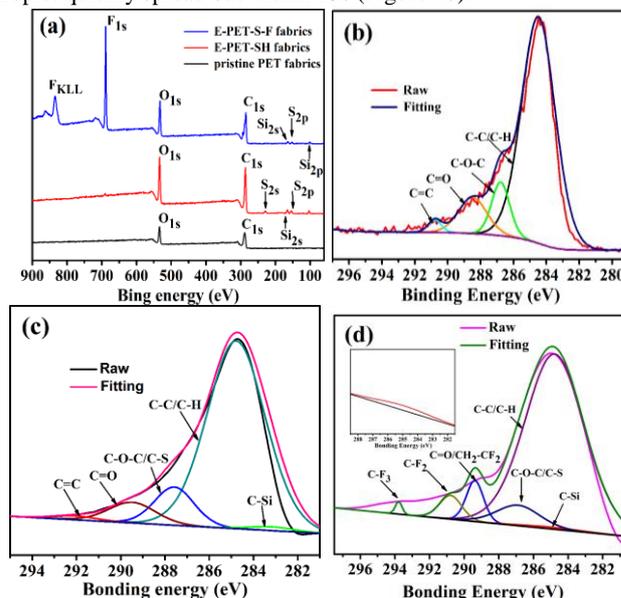
**Figure 2.** SEM images of (a) pristine PET, (b) E-PET, (c) E-PET-SH and (d) E-PET-S-F fabrics.

The chemical composition of the fabric surfaces by XPS was shown in Figure 3. The surface of pristine PET fabric shows the C 1s and O 1s signals, while the surfaces of E-PET-SH and E-PET-S-F dominate new Si, S and F signals (Figure 3a). This demonstrated that MPTES and DFMA were successfully incorporated onto the surface of the PET fibers. Figure 3(b) shows the C 1s core-level spectra of pristine PET fiber can be curve-fitted into four peak components with binding energies (BEs) at about 284.6, 286.6, 288.7 and 290.7 eV, attributable to the C–H, C–O–C, C=O and C=C of benzene species, respectively. Si (Si 2s 166.08 eV, Si 2p 103.08 eV) and S (S 2s 286.08 eV, S 2p 166.08 eV) signals, characteristic of covalently bonded Si and S, appeared in the E-PET-SH fabrics. The weak Si and S signals for the E-PET-SH surfaces is consistent with the nature of the single MPTES monolayer on the E-PET-SH fabric surface.<sup>59–61</sup> And a new curve-fitted peak component with BE at about 284 eV appeared attributable to C–Si. Figure 3(d) corresponds to the C 1s core-level spectra of E-PET-S-F fabrics. Different with Figure 3(b) and (c), the sample displayed new peaks belonging to C–F<sub>3</sub> (293.6 eV) and C–F<sub>2</sub> (290.5 eV). The above results indicated that DFMA have been successfully grafted on the fabric.

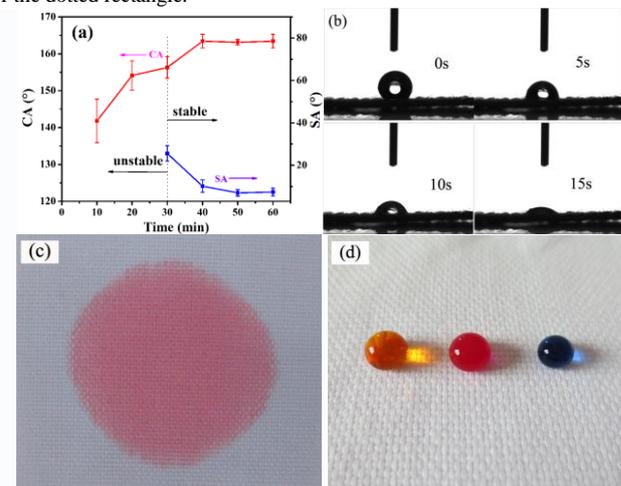
### Hydrophobic Property of the Thiol-Ene Click Chemistry Modified Fabrics

Figure 4 shows that the hydrophobicity of the E-PET-S-F is dependent on the reaction time, and the CA with water is stable and greater than 150° when the reaction time exceeded 30 min. When the reaction was prolonged over 40 min, the CA increased greater than 160° with decrease of SA lower than 10°. Meanwhile, the CA and SA did not alter significantly after reaction of 50 min, indicating saturation of hydrophobic moieties on PET fabrics. All of these

indicated that, when the amount of MPTES and DMPA were constant, the reaction of 50 min is enough to convert the hydrophilic fabrics (Figure 4c) to superhydrophobic ones (Figure 4d) with CA of 163.5  $\pm$  1° and SA of 7  $\pm$  2° making water droplets roll easily. By contrast, mercapto silane modification and click chemistry hydrophobization was also done on original PET fabrics without etching pretreatment under the same reaction conditions to obtain PET-S-F fabrics. The CA of PET-S-F fabrics was unstable and water droplet quickly spread out within 15s (Figure 4b).



**Figure 3.** (a) XPS spectra of the pristine PET, E-PET-SH and E-PET-S-F fabrics; C1s XPS spectra with fitting curves of (b) pristine PET, (c) E-PET-SH, and (d) E-PET-S-F; the inset in (d) shows the higher magnification view of the dotted rectangle.

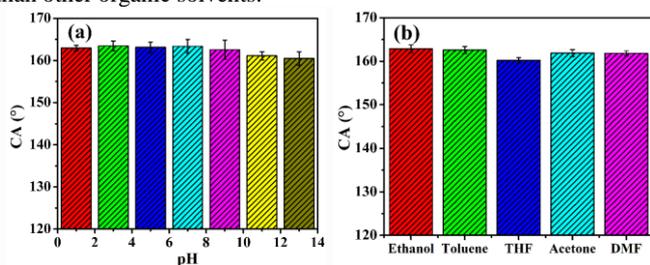


**Figure 4.** (a) The relationship between the CA/SA of E-PET-S-F and reaction time, (b) shape of a water droplet on the PET-S-F samples at different times in the case of an unstable hydrophobic state; Digital images of dyed water droplets after contacting (c) pristine and (d) E-PET-S-F fabrics.

### Stability of the Superhydrophobic Fabrics

Forming covalent bonds between fibers and low-surface-energy compounds is considered to be an effective way to enhance durability of the superhydrophobicity. The chemical durability and robustness of the superhydrophobicity were evaluated based on the

variations in the water repellency of the E-PET-S-F fabrics that were exposed to different conditions over time. We dipped the sample in solutions with different pH (pH = 1-13) for 72 h. Figure 5(a) shows that the CA of the superhydrophobicity changed little, indicating strong resistance to different pH solutions. This phenomenon may be due to the air layer trapped on the surface (Figure 6) which can inhibit the attack of acid or alkali. Additionally, immersion for 72 h of the superhydrophobic E-PET-S-F with various organic solvents did not make great change of the CAs (Figure 5b). The CAs of the samples remained above  $155^\circ$  although the superhydrophobic E-PET-S-F fabrics showed weaker resistance against THF solution than other organic solvents.

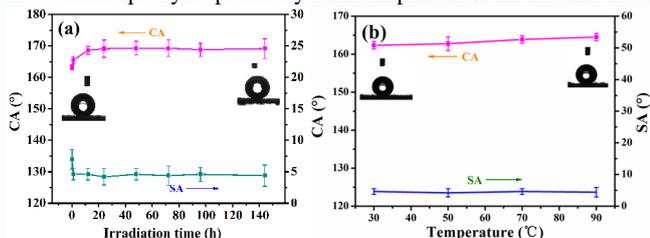


**Figure 5.** CAs of the E-PET-S-F fabrics treated by (a) immersion in different pH solutions for 72 h, (b) immersion in various organic solvents for 72 h.



**Figure 6.** Immersion of the E-PET-S-F (upper) and pristine (lower) fabric stuck on glass into water.

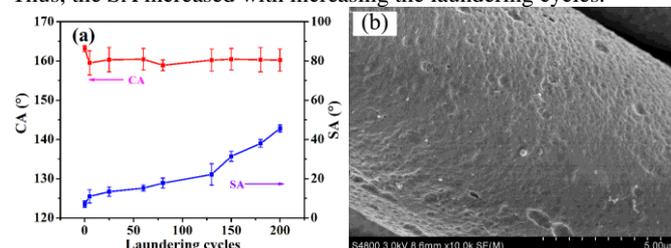
Meanwhile, chemical durability of E-PET-S-F fabric was also examined by exposing to severe conditions. For example, surface wettability examination showed that liquid droplets of 40% sodium hydroxide solution maintained spherical on the E-PET-S-F fabric. And after alkali etching of the E-PET-S-F fabric, the dyed water maintained spherical on the surface with the CA unchanged (see ESI Fig. S1† and S2†) due to its non-wetting properties. We also immersed the E-PET-S-F fabric into 40% sodium hydroxide solution varied from 0.5 to 12 h, the results were shown in ESI Fig. S2†. After immersing 12 h, the E-PET-S-F fabric was etched and worn out especially at the edge of the fabric which might be due to the attacking of alkali on the hydrophilic ends of fibers, but the CA on the surface changed little with the extension of soaking time. In contrast, the pristine PET fabric was totally dissolved after soaking 12 h in 40% sodium hydroxide solution. This means rendering the PET fabric superhydrophobicity could improve its alkali resistance.



**Figure 7.** CA and SA changes of superhydrophobic E-PET-S-F fabrics with (a) UV irradiation time and (b) temperature.

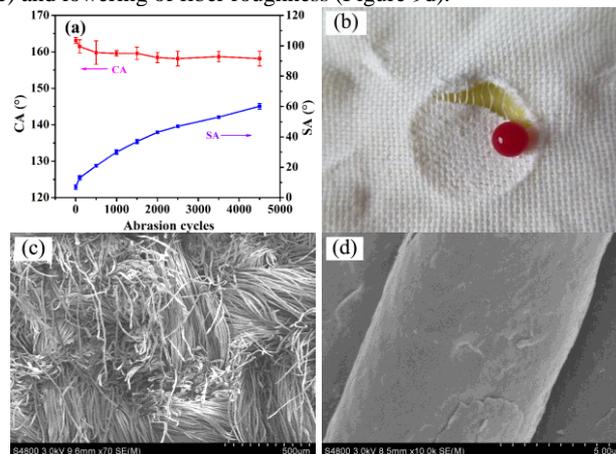
Figure 7(a) shows the CAs of E-PET-S-F fabrics as a function of UV irradiation time. It was found that the CA increased a little from  $163.5 \pm 1^\circ$  to  $167.2^\circ$  after the first 24 h which might be due to the migration of fluoroalkyl chains caused by heating effect under UV exposure. However, the CA and SA showed no great change for further irradiation, indicating excellent resistance of the E-PET-S-F to UV light. Additionally, stability test for different temperature was also conducted. The results showed that CA almost unchanged indicating excellent temperature stability (Figure 7b).

The influence of ambient force on the stability and robustness of the surfaces of superhydrophobicity is one of the most important factors that need to be considered for daily applications. Such resistance against mechanical damage was further evaluated by laundering samples of the E-PET-S-F in water with 0.37 wt% of detergent. It was found that the CAs changed only slightly after laundering for 40 cycles, approximate to 200 cycles of commercial laundering. However, SA increased from  $7 \pm 2^\circ$  to  $45.2 \pm 2^\circ$ , as shown in Figure 8(a). There are two reasons for this phenomenon. On the one hand, as laundering cycles increases, the roughness on the E-PET-S-F fiber surface decreased (Figure 8b) due to mechanical action. On the other hand, with severe mechanically laundering, some protruding fuzzes appeared on the surface of the sample, causing some force or adhesion to the water on the fabric. Thus, the SA increased with increasing the laundering cycles.



**Figure 8.** (a) Changes of CA and SA of E-PET-S-F with washing cycles, (b) SEM image of E-PET-S-F after laundering test of 200 cycles.

In order to measure the durability against the mechanical stress, a standard procedure of the abrasion test was performed on the samples of E-PET-S-F according to a modified procedure based on the AATCCA Test Method 8-2001.<sup>34-35, 39, 41</sup> The applied pressure was 45 kPa and the results were shown in Figure 9. It was found that the CA of the E-PET-S-F fabrics decreased from  $163.5 \pm 2^\circ$  to  $157 \pm 3^\circ$  (Figure 9a), indicating excellent durability of superhydrophobicity against abrasion although the samples were worn out (Figure 9b). As for SA, it increased from  $7 \pm 2^\circ$  to  $60 \pm 2^\circ$ , which might be due to the formation of surface protrusions (Figure 9c) and lowering of fiber roughness (Figure 9d).<sup>35, 39</sup>

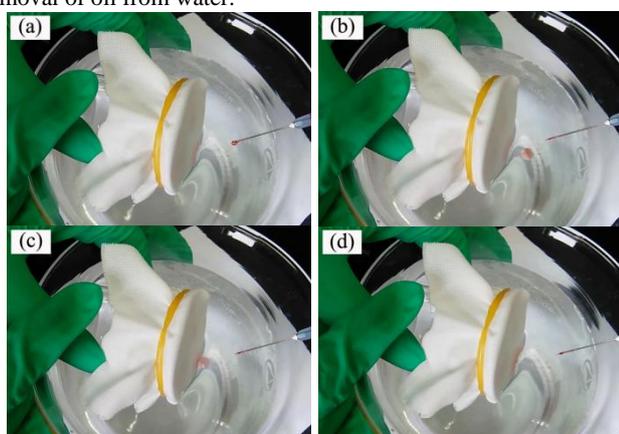


**Figure 9.** (a) Changes of CA and SA of E-PET-S-F fabrics with abrasion cycles, (b) photograph of a water droplet on the E-PET-S-F fabrics after 4500 cycles, (c) SEM image of E-PET-S-F fabrics after abrasion test of 4500 cycles; (d) Higher magnification of (c).

It should be noted that the durability test experiment is with very strong mechanical force and much more cycles during washing or abrasion in order to challenge the stability of the property of the as-obtained fabrics. Although the effect of roughness changes induced gradual transition of hydrophobicity from a Cassie-Baxter to a Wenzel state and subsequently loss of repellence occurred in the materials, the fabrics still maintained superhydrophobicity.

### Oil/Water Separation.

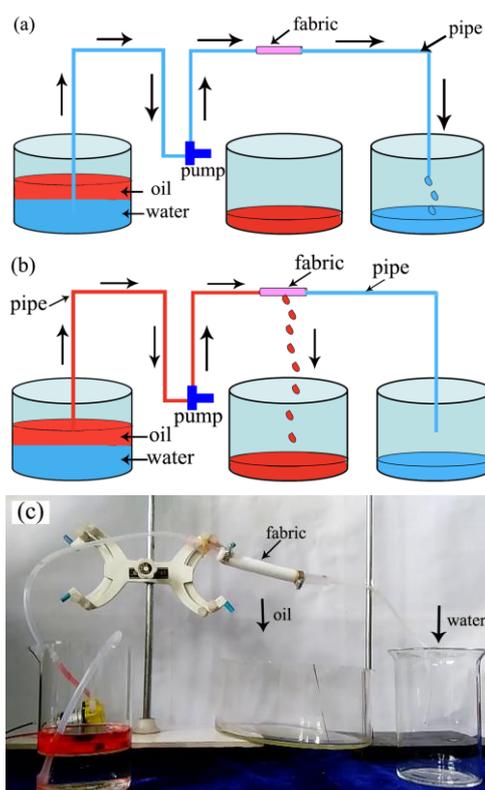
Superhydrophobic fabrics are promising oil/water separation materials for practical applications. A beaker covered with a piece of E-PET-S-F fabric was sunk into water partially, and n-hexane dyed with Sudan II was dropped onto the water surface to form a thin layer near the fabric. It was found that n-hexane layer was fully absorbed within a few seconds, leaving a transparent region on the water surface (Figure 10a-d and video S1). This shows that the E-PET-S-F fabric possesses simultaneous superhydrophobicity and superoleophilicity, making it very promising as the material for removal of oil from water.



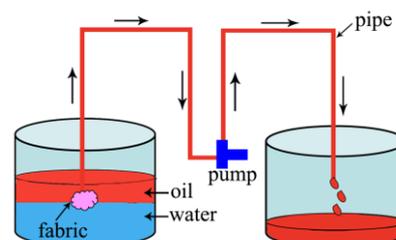
**Figure 10.** (a)-(d) Photographs of the self-driven oil/water separation at different temporal stages.

Only absorbing oil from water is not enough for the solutions to oil spill accidents, and it is still necessary to design oil skimmer and separation devices toward separating oil-water mixtures. Based on the different behavior of the E-PET-S-F fabrics towards oil and water, a bench-scale oil/water separation apparatus was built up (Figure 11 and video S2). As shown in Figure 11, E-PET-S-F fabrics were rolled as a part of the conduit. After turning on the self-priming pump, water can successfully pass through the rolled fabrics as a tube to the water collector and the n-hexane will leak at the part of E-PET-S-F fabrics to the oil collector due to the superhydrophobicity and superoleophilicity special wetting properties. Importantly, this process is repeatable (video S2).

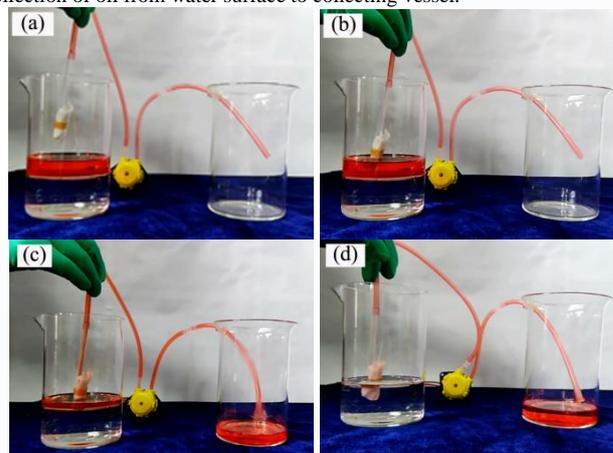
We also adopted the design of the oil-water separation apparatus commonly reported in literatures using superhydrophobic materials at the entrance head of pipe,<sup>62-63</sup> as shown in Figures 12. N-hexane could be selectively absorbed when immersing the E-PET-S-F fabrics into the n-hexane/water mixture. After turning on the self-priming pump, the n-hexane absorbed by the E-PET-S-F fabrics was pumped to collecting vessel. At the meantime, n-hexane around the E-PET-S-F fabrics was consecutively sucked in. When the n-hexane on the water surface disappeared, the n-hexane above the nozzle of the pipe in the E-PET-S-F fabrics was further pumped away and an air channel formed in the E-PET-S-F fabrics to terminate the n-hexane collection. In the pumping process, 100 mL of n-hexane was collected from the water surface, and no water was observed in the collection vessel, thus showing the high oil/water separation efficiency and oil recovery rate of this system (video S3 and Figure 13).



**Figure 11.** Schematic diagram of experimental set-up for oil/water separation. (a) If the pipe immersed into water, the water can successfully pass through the rolled fabric to the water collector; (b) If the pipe immersed into oil, the oil will leak from fabric to oil collector; (c) Photographs of the oil/water separation apparatus with n-hexane (dyed in red).



**Figure 12.** Schematic diagram of experimental set-up for consecutive collection of oil from water surface to collecting vessel.



**Figure 13.** (a)-(d) Photographs of the continuous oil collection from a water surface at different temporal stages.

## Conclusions

In summary, we have demonstrated a simple and novel strategy to fabricate superhydrophobic surfaces, namely, combination of chemical etching of PET fibers with thiol-ene click chemistry hydrophobization of PET fabrics. It was shown that the superhydrophobicity of the modified fabrics is resistant to UV irradiation, chemical etching, mechanical laundering and abrasion. Importantly, the surface of the superhydrophobic fabrics showed potential application in water/oil separation. This method might be suitable for other hydrophobic monomers for fabrication of superhydrophobic fabrics, paving a way for generating durable and robust superhydrophobic surfaces through chemical bonding between the hydrophobic substances and the substrates. Importantly, the method is simple and suitable for large-scale production.

## Acknowledgements

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Superhydrophobic fabrics were fabricated by alkali etching of fibers, modification with mercapto silanes and hydrophobization via thiol-ene click chemistry.

