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Preparation of Superhydrophobic Fabric Based on Dopamine and Michael Addition under Ultraviolet Light

Baoliang Wang, Lili Xing, Tieling Xing, and Guoqiang Chen*

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ABSTRACT: This work reports a simple, stable, and environmentally friendly method to prepare durable superhydrophobic surfaces. First, a polydopamine coating is formed by oxidative polymerization of dopamine to form a secondary reaction platform to provide reaction sites for subsequent experiments. We applied a polydopamine layer onto a fiber surface using the Michael addition-reaction-grafted tetrakis (3-mercaptopropionic acid) pentaerythritol ester, followed by the introduction of tetraallyl silane and (mercapto) methyl siloxane-dimethyl siloxane copolymer on the polydopamine by a thiol−ene click-reaction under ultraviolet light. The resulting superhydrophobic Nylon 56 fabric exhibited a 166° static contact angle as well as excellent stability. The surface morphology of all samples was observed by field emission scanning electron microscope, X-ray photoelectron spectroscopy and energy dispersion spectroscopy, and the elemental composition and surface chemical state of the samples were analyzed. It also had the ability of oil-water separation. Fabric with such benefits broadens the applicability and innovation of superhydrophobic textiles for environmental and industrial applications.
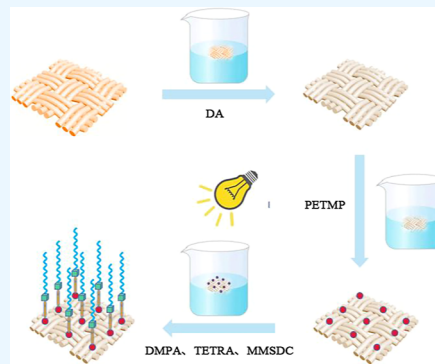
1. INTRODUCTION

The unique wettability of superhydrophobic surfaces[1,2] attracts wide attention from scientists and engineers searching for innovative solutions for issues related to corrosion protection, and ice accumulation,[3,4] a need for self-cleaning and oil−water separating surfaces[5,6] as well as for applications associated with antifouling, microfluid transportation, etc.[7] However, among the many superhydrophobic surface preparation processes, the sol−gel method can adapt to the surfaces of different substrates, but the cost is expensive.[8] The coating prepared by the etching method has good mechanical properties, but it is easy to be destroyed in strong acid and alkali environments,[9] and the template method cannot be used in industrial applications because of its complicated preparation process.[10] Under ultraviolet irradiation, the preparation of superhydrophobic surfaces by the thiol−ene click reaction has attracted great attention, in which C=C functional groups react with thiol functional groups on the surface. The click reaction of thiol−ene induced by ultraviolet light has the advantages of fast reaction rate, environmental protection, high yield, and simple operation and is considered as an effective method of chemical modification.[11,12] In an attempt to solve all of these issues, this work developed a simple, rapid, environmentally friendly, and pollution-free method of preparation of superhydrophobic surfaces.

Surface deposition technology based on mussel[13] bionics is a recently developed material surface modification method, and dopamine is also being sought after by an increasing number of scientists. In a weakly alkaline environment, dopamine can undergo oxidative self-polymerization and polydopamine can be formed on the surface of various substrates. Polydopamine can be easily oxidized to form active quinone, which can react with various functional groups including mercaptan and amine through Michael addition or a Schiff base reaction to form covalently grafted functional coatings. The reaction with molecules containing amine or mercaptan is easy and easy to operate. The polydopamine layer is also used as an interface layer for postmodification and allows the coating to be further modified by other functional materials such as nanoparticles, oligomers, or polymers. Based on the inherent advantage of polydopamine as a primer in conjunction with lignin to build a hydrophobic substrate, Jiang et al. produced a low surface energy buffer layer to prevent water penetration.[14] Yang et al. incorporated TiN/polydopamine nanoparticles onto the polydopamine sponge by using hydrolytic methyltrimethoxysilane to endow it with solar-absorbing capability. The addition of these nanoparticles not only reduced assembly energy barriers but also enhanced hydrophobicity and stability.[15] Polydopamine's strong adhesion properties provide the modified technology unparalleled versatility.[16−18] It can be
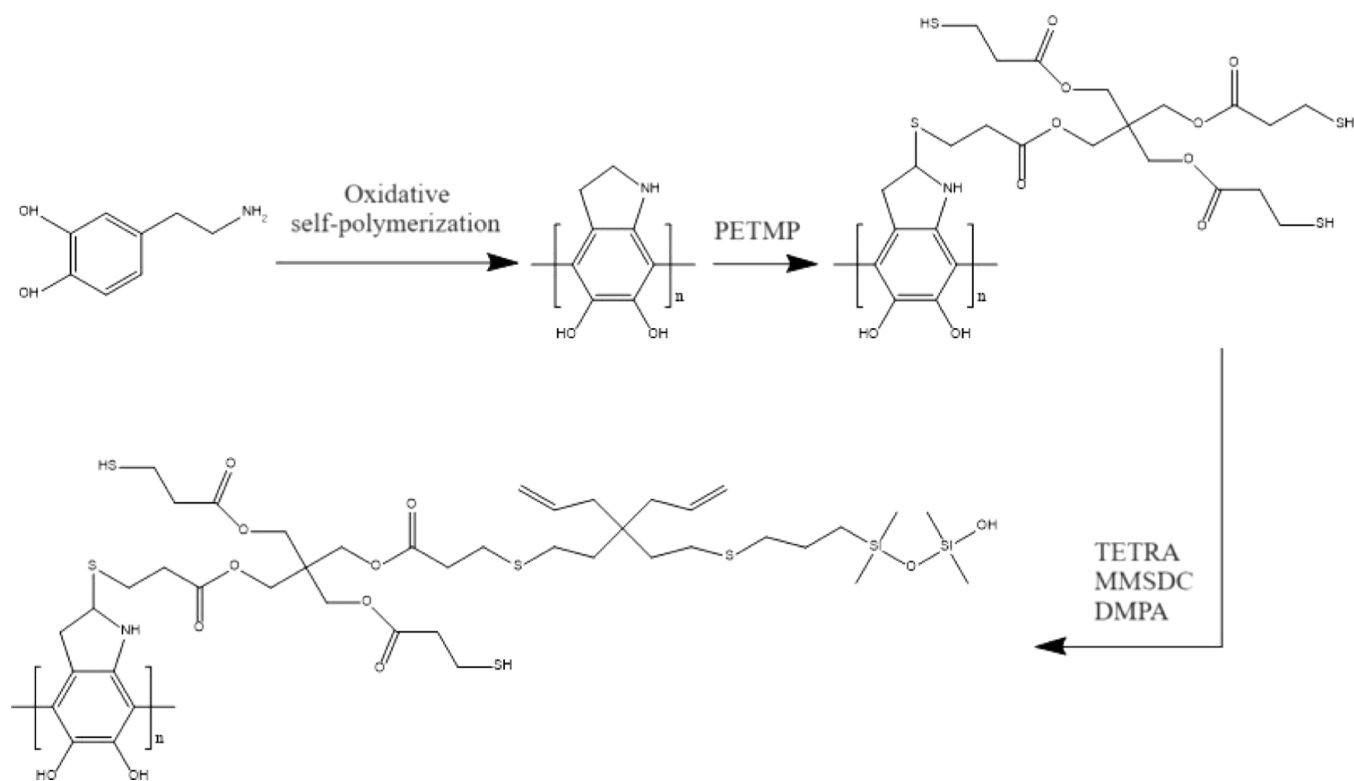
Figure 1. Formation mechanism of Nylon 56 functionalization to create a superhydrophobic fabric.
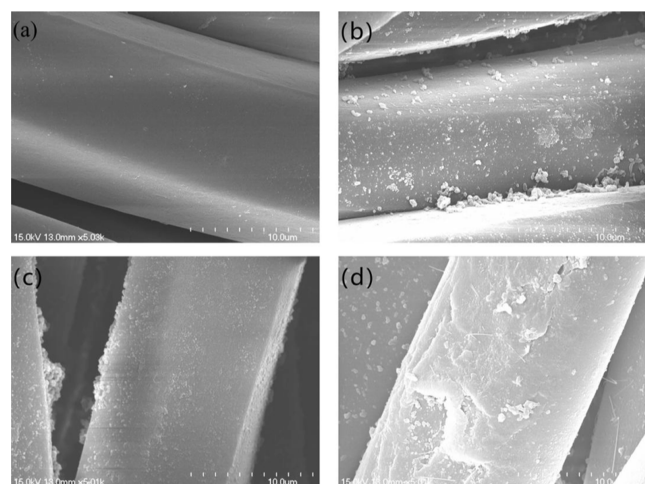

Figure 2. SEM micrographs of the (a) original and (b) dopamine-, (c) sulfhydryl-, and (d) mercapto-alkene-modified Nylon 56 fabric.

Table 1. Element Composition Content of (a) Original Nylon 56 Fiber, (b) Dopamine-Modified Nylon 56 Fiber, (c) Sulfhydryl-Modified Nylon 56 Fiber, and (d) Superhydrophobic Nylon 56 Fiber

element	C	O	N	S	Si	total
(a) (weight %)	44.732	40.314	14.954	0	0	100
(b) (weight %)	56.618	15.423	27.959	0	0	100
(c) (weight %)	50.460	30.779	16.605	2.156	0	100
(d) (weight %)	60.236	15.467	19.854	2.323	2.12	100

deposited on the surfaces of polymers, metals, metal oxides, and even low-surface-energy polytetrafluoroethylene. What researchers are most excited about is this technology's postfunctionalization capability as a secondary reaction platform, which provides a high degree of freedom and maneuverability for constructing functional materials.

We used Nylon 56 as the base material, which was then coated with polydopamine (by oxidative in-solution polymerization of dopamine) for subsequent functional grafting. First, we grafted the polymeric film (using a Michael addition reaction) with multiple sulfhydryl functional groups and then introduced tetraallyl silane (TETRA) and (mercapto)-methylsiloxane-dimethylsiloxane copolymer (MMSDC) into the modified fibers by a sulfhydryl-olefin click reaction. The resulting superhydrophobic fabric exhibited excellent physical and chemical stability.

2. EXPERIMENTAL DETAILS

2.1. Initial Chemicals. Nylon 56 fabric was purchased from Jiangsu Lianfa Textile. Dopamine hydrochloride (DA, 98.5%) was purchased from Shanghai Yuanye Biotechnology. Trimethylaminomethane, tetra (3-mercaptopropionic acid) pentaerythritol ester (PETMP) was supplied from Shanghai Jingchun Biochemical Technology. TETRA was acquired from Shanghai Saen Chemical Technology. MMSDC was from Shanghai Aladdin Biochemical Technology. Trimethyl-aminomethane hydrochloride was provided by Suzhou Gretel Pharmaceutical Technology. 2,2-dimethoxy-2-phenyl acetophenone (DMPA), absolute ethyl alcohol, oil O, methylene blue, dichloromethane, ethyl acetate, carbon tetrachloride, and dimethyl sulfoxide (DMSO) were supplied by Sinopharm Chemical Reagent.

2.2. Preparation of Dopamine-Modified Fabric. 0.4 g of dopamine was dissolved in 200 mL of deionized water, after which the pH value was adjusted to 8.5 with trimethylolaminomethane and trimethylolaminomethane hydrochloride. A 5 × 5 cm piece of Nylon 56 fabric was then placed into the solution
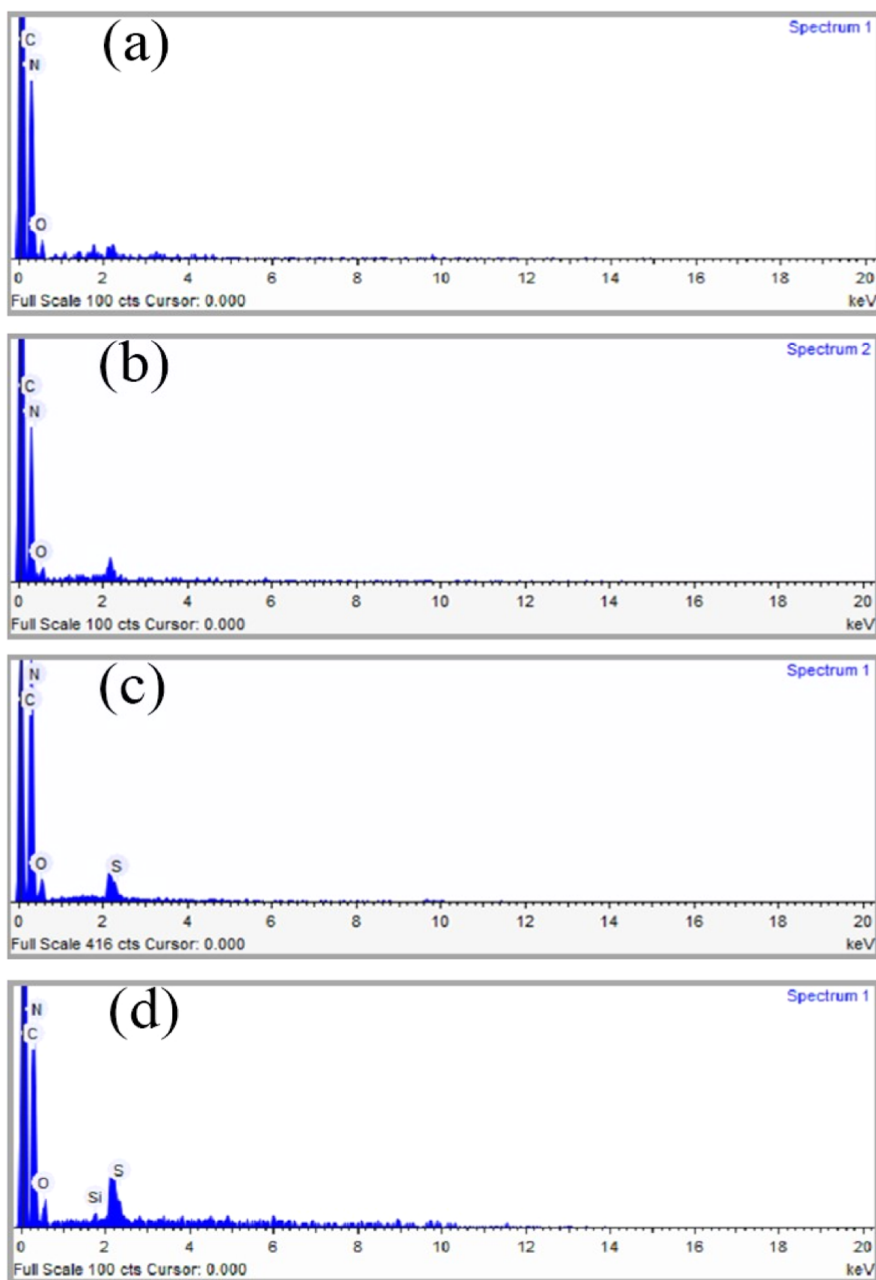
Figure 3. EDS spectra of (a) original Nylon 56 fiber, (b) dopamine-modified Nylon 56 fiber, (c) sulfhydryl-modified Nylon 56 fiber, and (d) superhydrophobic Nylon 56 fiber.

and then into a low-noise oscillating dyeing machine (set at 45 °C) for 12 h. After this, the fabric was ultrasonicated in ethanol to remove unreacted and excessive polydopamine and then dried at 60 °C for 0.5 h. The final material was dopamine-modified Nylon.

2.3. Preparation of Mercapto-Modified Fabric. One gram of PETMP was dissolved in 100 mL of dimethyl sulfoxide in an Erlenmeyer flask, after which the dopamine-modified fabric was added, and the whole mixture was placed into a noise-shaking dyeing machine (set at 30 °C) for 2 h. The obtained piece of fabric was rinsed with absolute ethanol and then dried at 140 °C in a vacuum.

2.4. Preparation of Superhydrophobic Fabric. The mercapto-modified fabric was soaked in 150 mL of ethyl acetate solution, after which 0.19 g of TETRA, 0.66 g of MMSDC, and 0.25 g of DMPA were added. The container was

then sealed and exposed to an ultraviolet (UV, with λ = 365 nm) 250 W light source (for 30 min) placed 15 cm away from the fabric piece. After the first 15 min of UV light exposure, the fabric was turned to the other side to ensure an even exposure of both sides to the UV light. After that, the material was rinsed with absolute ethanol and dried at 140 °C for 1 h to obtain a superhydrophobic material.

3. RESULTS AND DISCUSSION

3.1. Brief Description of the Formation Mechanism of Superhydrophobic Fabric. First, dopamine oxidatively self-polymerized in the aqueous solution, forming dispersed polydopamine aggregates, which underwent free Brownian motion in the aqueous solution, eventually adhering to the fabric fibers coating them. Then, during the second step,
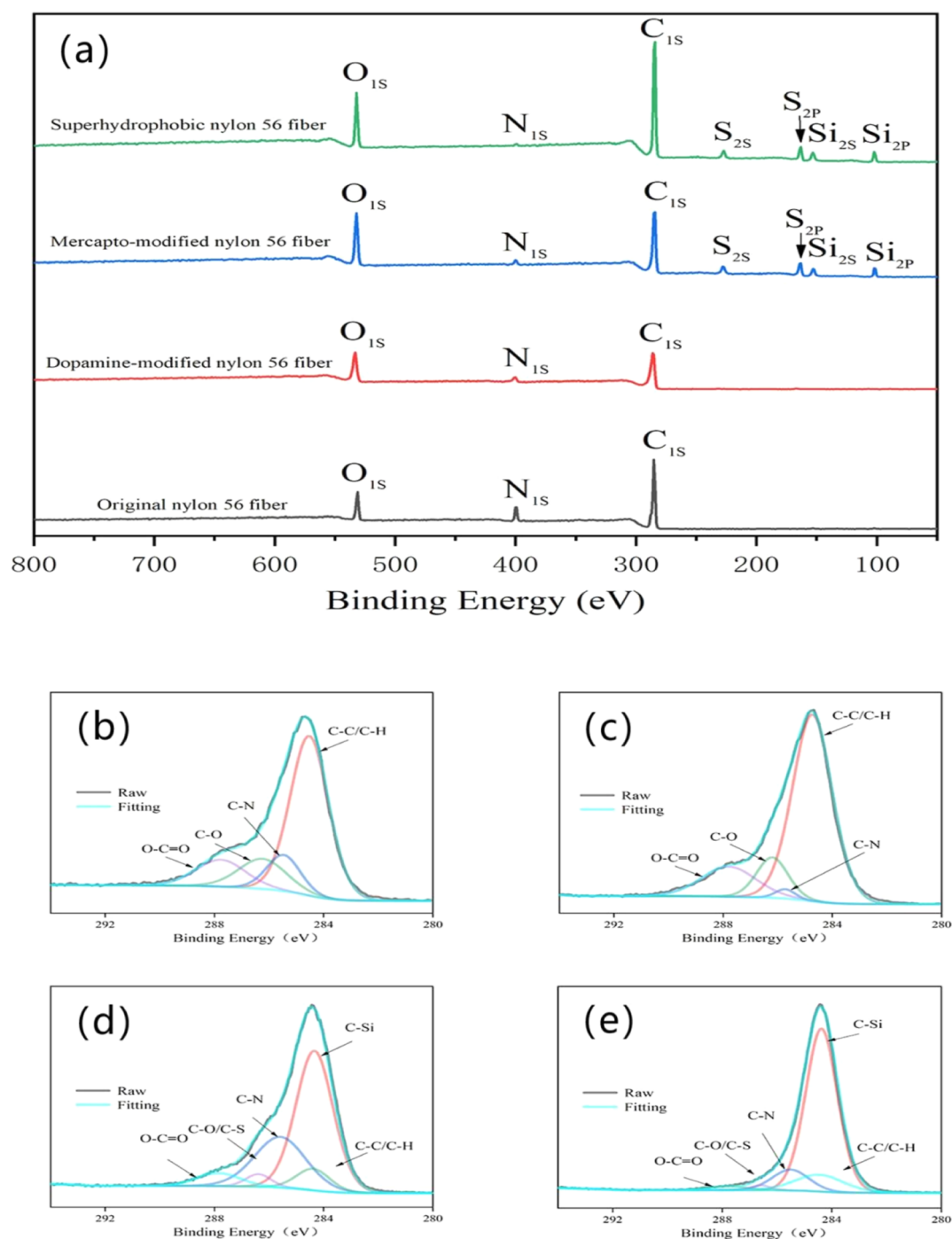
Figure 4. Survey (a) and high-resolution (b−e) XPS spectra of the original fabric (a, b) as well as fabric modified with dopamine (c), sulfhydryl (d), and TETRA/MMSDC grafting (e).

PETMP and polydopamine were covalently cross-linked through a Michael reaction, which modified the fabric surface with numerous sulfhydryl groups. Third, UV exposure to light and photoinitiator action forced TETRA to react sequentially with the surface sulfhydryl groups on the polydopamine-modified coating. Simultaneously, MMSDC was grafted onto the alkenyl group of TETRA by thiol-alkene click chemical reaction, which attached hydrophobic and low-surface-energy groups to the fabric, yielding a superhydrophobic surface (the superhydrophobic reaction mechanism is shown in Figure 1).

3.2. Surface Morphology and Composition of the Superhydrophobic Fabric. Scanning electron microscopy (SEM) analysis of the original fabric revealed a smooth surface (Figure 2a). After Nylon 56 was modified with polydopamine, aggregates of micro- and nanoparticles formed on the surface (see Figure 2b). Michael's reaction resulted in the grafting of PETMP onto Nylon 56, which translated into a formation of a series of closely arranged block polymer particles (see Figure 2c), which roughened the surface of the Nylon 56 fibers significantly. After exposure to UV light, an A coating with low surface energy was formed on the surface of Nylon 56 (see Figure 2d) due to the formation of a thick polymeric film on its surface. This dense network formed as a result of the
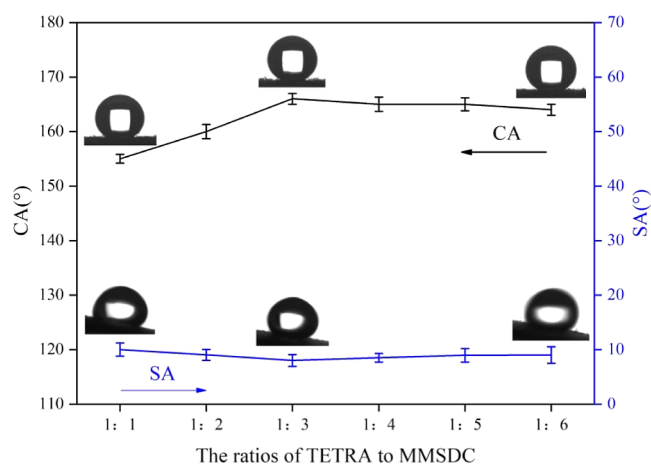
Figure 5. Changes in CA and SA correspond to the ratios of TETRA to MMSDC.
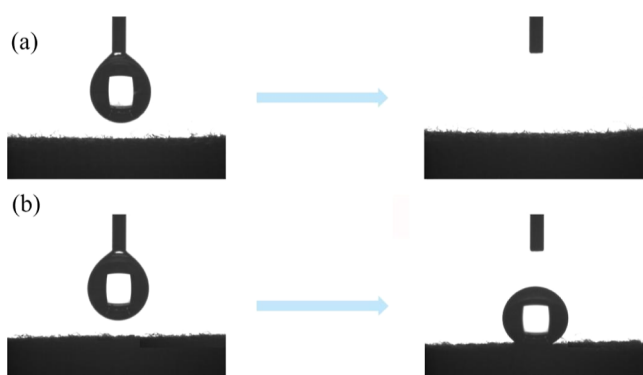

Figure 6. Wettability tests of the original (a) and modified superhydrophobic (b) fabric.

incorporation of low surface energy mercapto-alkene groups into the fabric surface by click-reaction.

The energy-dispersive spectrometry (EDS) energy spectra of Nylon 56 fibers before and after finishing are shown in Table 1 and Figure 3. Table 1b shows that the proportion of N content in dopamine-modified Nylon 56 fibers has increased significantly, indicating that polydopamine was successfully coated on the table's surface. PETMP was successfully deposited on the polydopamine coating, as evidenced by the appearance of element S in Table 1c. Furthermore, the newly appeared Si element on Nylon 56 fiber (Table 1d) evidences that the thiol−ene click chemical reaction was successful. The low-surface-energy hydrophobic polymer has been grafted to the fiber's surface and has been formed on the fabric's surface.

X-ray photoelectron spectroscopy (XPS) of the original Nylon 56 showed C, O, and N peaks (see Figure 4a). XPS of the fully modified fabric showed additional peaks at 150.5, 100.1, 229.0, and 164.0 eV, which were attributed to the Si 2s, Si 2p, S 2s, and S 2p energy bands, respectively. These results indicate that S-containing low surface energy groups were successfully attached to the Nylon 56 surface by a click-coupling reaction. The C 1s peak in the XPS curve recorded for the original fabric was deconvoluted into subpeaks at 284.6, 285.7, 286.5, and 288.2 eV, which correspond to the C−C/C−H, C−N, C−O, and O−C═O bonds, respectively (see Figure 4b). The appearance of the peak corresponding to the C−N bond in the dopamine-modified fabric confirmed polydopamine adsorption on the Nylon 56 surface. After Michael's

reaction (which resulted in grafting the sulfhydryl functional groups to the Nylon 56 surface) followed by the click-reaction, the Nylon 56 fibers were grafted with TETRA and MMSDC, which translated into the appearance of the XPS peaks at 286.5 and 284.9 eV (see Figure 4c−e), which correspond to C−S and C−Si bonds.

3.3. Influence of the Ratio of Reactants on the Superhydrophobic Finishing of Fabrics. Herein, PETMP and MMSDC were sequentially grafted via the thiol−ene click reaction and low-surface-energy substances were introduced on the fiber surface. TETRA and MMSDC are highly hydrophobic reagents, and the dose ratio between them has a significant influence on the wettability of the fabric surface. Figure 5 shows the relationship between CA and SA and the TETRA/MMSDC ratios. When the molar mass ratio of the two is 1:3, the static contact angle is 166°, the sliding angle is 7.5°, and the superhydrophobic performance is optimal. This is attributed to PETMP already occupying one double bond, leaving three double bonds available. MMSDC is in charge of the grafting point. It embodies click-chemistry modular properties. The CA did not rise upon an additional increase in the amount of MMSDC. This could be because the sulfhydryl polymer on the fiber has reached a saturated state, and all the double bond grafting points have been occupied. These results show that the best superhydrophobic performance is achieved when the molar mass ratio of TETRA to MMSDC is 1:3.

3.4. Wettability Tests of the Superhydrophobic Fabric. The wettability of our modified fabric was tested by using a static contact angle technique. A deionized water droplet completely penetrated the original fabric (see Figure 6a). However, the droplets on the superhydrophobic fabric remained spherical and stayed on the fabric surface (see Figure 6b) at the 166° angle. Thus, our 3-step fabric modification significantly decreased the fabric permeability by water and yielded a superhydrophobic effect.

3.5. Mechanical Stability of the Superhydrophobic Fabric. Taking current industrial production requirements into account, the mechanical stability of the superhydrophobic fabric determines the durability and resistance to external forces. Thus, we used a sandpaper abrasion test to quantitatively analyze the mechanical durability of the superhydrophobic fabric. The fabric was placed on 1000-Cw sandpaper, pressed with a weight of 500 g, and was then pulled 15 cm along the ruler, as shown in Figure 7a. To demonstrate the change in wettability, static CA and SA were recorded after every five wear cycles (Figure 7b). The CA of the fabric dropped from 166 to 151° subsequent to five wear cycles. This could be because the low-surface-energy polymer was grafted with the polydopamine coating via strong chemical bonds and the polydopamine coating and fiber were then bonded together. The substrate's super adhesion makes it difficult for external forces to damage and peel it off.

3.6. Self-Cleaning Performance of the Superhydrophobic Fabric. Superhydrophobic fabrics exhibit exceptional antifouling and self-cleaning properties. When pollutants contaminate these fabrics, they can be easily removed by rolling water droplets. In this test, a reactive blue dye is used as a marker for the self-cleaning test. The blue dye in the original fabric does not move with the water droplets, as shown in Figure 8a,b; however, the pollution spreads over the entire fabric. Conversely, the contaminants on the superhydrophobic fabric are easily removed by the water droplets, leaving a clean
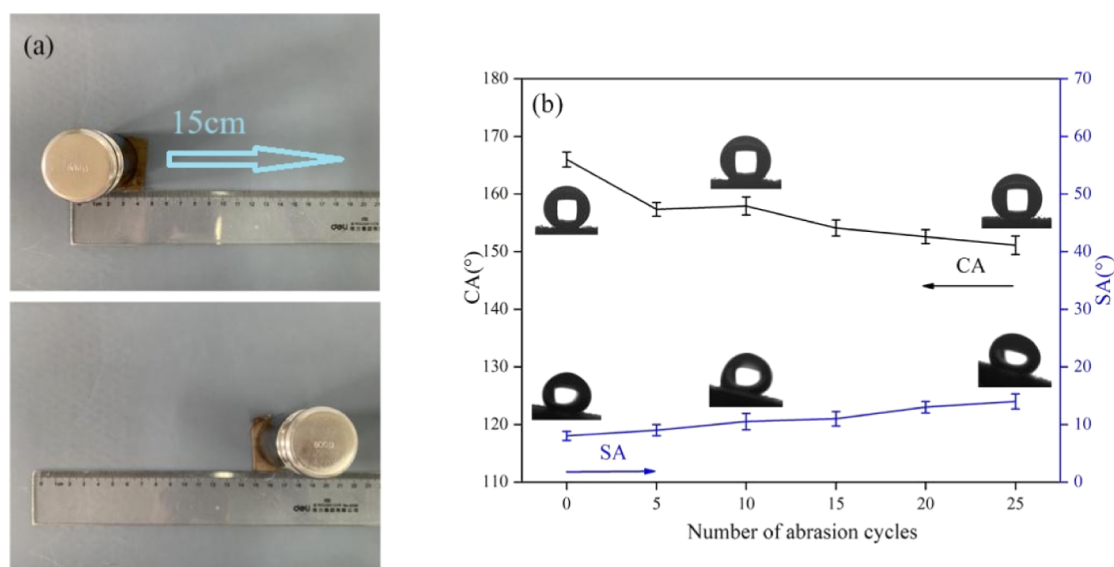
Figure 7. (a) Image of the sandpaper abrasion test. (b) Changes in the CA and SA of superhydrophobic fabrics subsequent to 25 abrasion cycles.
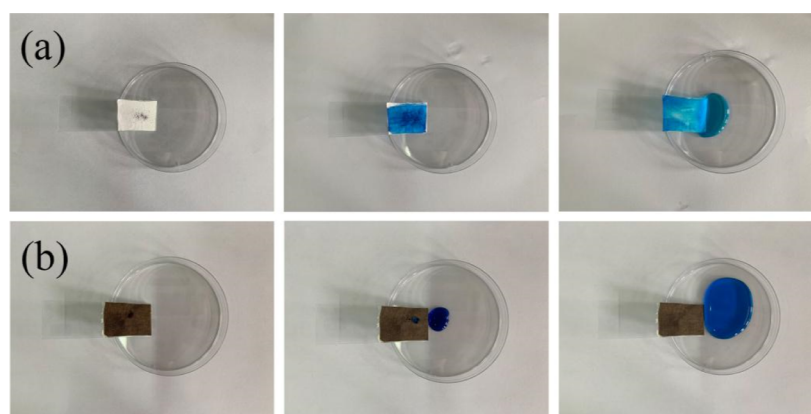

Figure 8. Self-cleaning test of fabric: (a) original fabric and (b) superhydrophobic fabric.

Figure 9. (a) Water soaking phenomenon of the original fabric and the superhydrophobic fabric, (b) state of different droplets on the original fabric, and (c) state of different droplets on the superhydrophobic fabric.

surface. To further demonstrate the superhydrophobic fabric's water repellency, both the original fabric and the super-hydrophobic fabric were immersed in water. The original fabric sank into the water, whereas the superhydrophobic fabric floated on the water's surface after being released (Figure 9a). Furthermore, to investigate the practicality of coated fabrics for everyday use, we performed antifouling tests with saltwater, coffee, milk, dyed water, cola, and tea. The original fabric was wholly polluted and wetted, as shown in Figure 9b,c; however, the droplets on the surface of the superhydrophobic fabric were spherical and three-dimensional. The test results show

that the modified fabric exhibits excellent self-cleaning and antifouling properties.

3.7. Oil–Water Separation Performance of the Superhydrophobic Nylon 56 Fabric. Superhydrophobic fabrics are widely used to alleviate marine oil pollution, because of their unique oil–water separation properties. Therefore, we tested the oil/water separation performance of our superhydrophobic fabric. For this purpose, we first dyed (with red color) methylene chloride and carbon tetrachloride with oil red O. After that, a piece of our superhydrophobic fabric was placed in the solution, containing these dyed chemicals (see Figure 10a,b). Our modified fabric completely
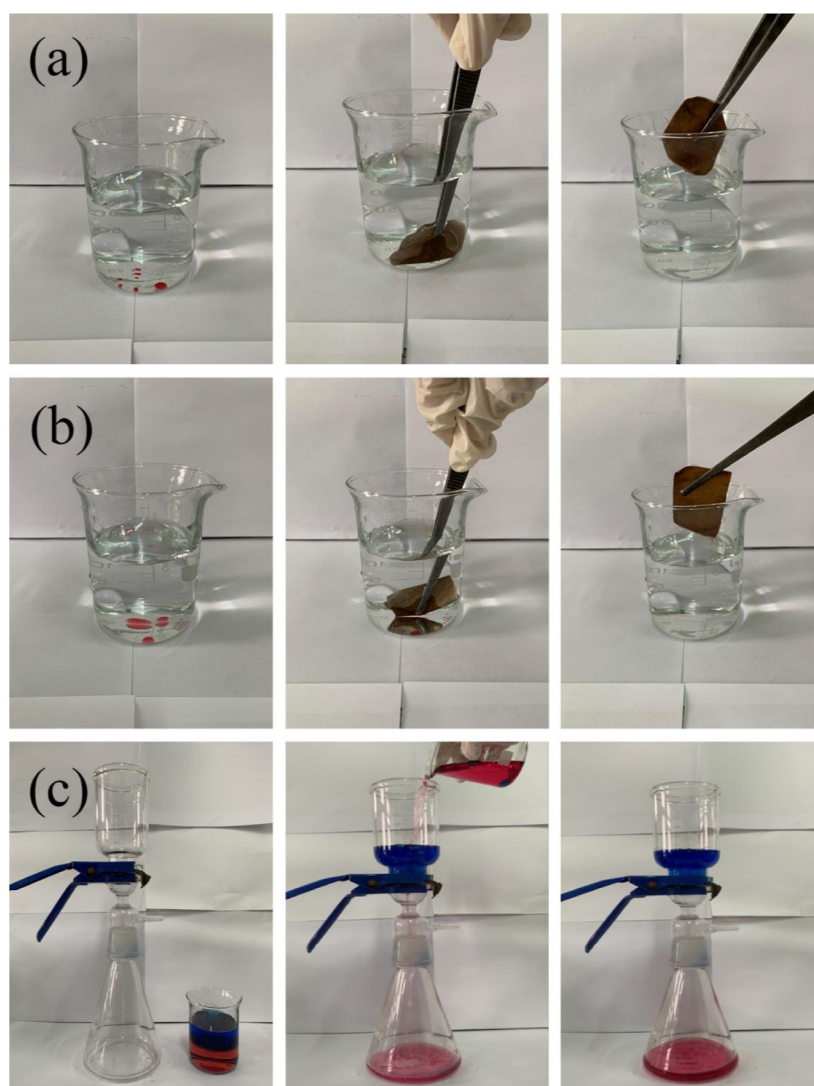
Figure 10. Selective adsorption of methylene chloride (a) and carbon tetrachloride (b), both dyed with oil red O, in water by the superhydrophobic fabric. (c) Oil−water separation test of the superhydrophobic Nylon 56 cotton interwoven fabric.
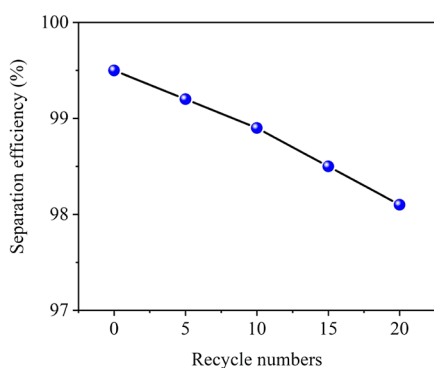

Figure 11. Oil−water separation test.

absorbed the red droplets (Figure 10a,b), proving that it is capable of adsorbing oil stains.

We then further tested the oil−water separation performance of our superhydrophobic fabric using a setup shown in Figure 10c. We inserted a 6 × 6 cm piece of the modified Nylon 56 into the oil−water separation flask. Then, dichloromethane and water were dyed with oil red O and methylene blue, respectively, and placed into the same beaker. The oil/water mixture (containing 100 mL of each liquid) was then poured through the filtration setup containing our superhydrophobic material. The red oil penetrated the fabric quickly, while blue water remained trapped by the fabric. In addition, in order to test the oil−water separation efficiency of the sample, we carried out the oil−water separation test for 20 cycles. At the end of each separation test, we calculate the separation efficiency by measuring the weight of the remaining water. As shown in Figure 11, the separation efficiency gradually decreases with the increase of the separation period. However, after 20 cycles, the separation efficiency is still high (above 98.0%). Thus, the superhydrophobic Nylon 56 fabric developed in this work possessed excellent oil−water separation ability and could be used to treat oil spills in water reservoirs.

4. CONCLUSIONS

This work reports the modification of Nylon 56 with oxidized and polymerized dopamine, further enriched (by a second-order reaction) with hydroxyl groups to attach polydopamine aggregates to the fabric surface. The resulting fabric was further

modified with the superhydrophobic groups, attached to the surface by a click coupling reaction involving PETMP, TETRA, and MMSDC, and grafted onto the polydopamine aggregates already present on the Nylon 56 surface by Michael addition reaction. This last modification step significantly increased the surface roughness of the fabric, which, in turn, substantially reduced its surface energy, allowing for super-hydrophobic properties. The static contact angle of our prepared superhydrophobic material was 166°. It also demonstrated excellent superhydrophobic stability and oil–water separation properties. Moreover, Nylon 56 itself has the advantages of environmental protection, high elasticity, high-temperature resistance, and wear resistance. All of these properties allow our novel modified Nylon 56 to become a strong candidate for environmental applications, involving water reservoir cleaning from oil and other organic pollutants. In addition, based on the superstrong adhesion of dopamine, the polydopamine coating formed by oxidative polymerization can be adsorbed on different substrates through its covalent bonds to form a secondary reaction platform, which can be endowed with superhydrophobic properties after grafting other low surface energy substances.

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Notes

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