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Robust, Self-Healing Superamphiphobic Fabrics Prepared by Two-Step Coating of Fluoro-Containing Polymer, Fluoroalkyl Silane, and Modified Silica Nanoparticles

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A robust, superamphiphobic fabric with a novel self-healing ability to autorepair from chemical damage is prepared by a two-step wet-chemistry coating technique using an easily available material system consisting of poly(vinylidene fluoride-*co*-hexafluoropropylene), fluoroalkyl silane, and modified silica nanoparticles. The coated fabrics can withstand at least 600 cycles of standard laundry and 8000 cycles of abrasion without apparently changing the superamphiphobicity. The coating is also very stable to strong acid/base, ozone, and boiling treatments. After being damaged chemically, the coating can restore its super liquid-repellent properties by a short-time heating treatment or room temperature ageing. This simple but novel and effective coating system may be useful for the development of robust protective clothing for various applications.

1. Introduction

Superamphiphobic surfaces have a contact angle (CA) greater than 150° to both water and oil fluids.[1] They are more desirable than those showing super-repellency only to water or oils because of the enhanced repellent performance to liquids,[2] and as such they show excellent promise in applications ranging from self-cleaning and anti-sticking to corrosion resistance, drag reduction, energy conversion and protection of electronic devices.[3–5] When fabrics have a superamphiphobic surface, they are not only super-repellent to water and oil fluids, but also breathable, which is useful for the development of protective clothing, besides the potential applications in the aforementioned fields. Despite the significant progress made in developing superamphiphobic surfaces so far, challenges still remain in making a surface superphobic to fluids with a surface tension below 35 mN/m.[6–9] Most liquid-repellent surfaces are low in durability and mechanical robustness.[10]

To improve the durability, several strategies have been developed, such as crosslinking the coating layer,[11–13] creating multi-scaled roughness on the substrate,[14] establishing chemical bonds between coating and substrate,[15,16] introducing a bio-inspired self-healing function,[17,18] or endowing the coating with an elastomeric nanocomposite structure.[19] Self-healing is of particular interest to improving durability because of the regenerating ability against chemical or physical damages. Self-healing superhydrophobic or superamphiphobic coatings on hard substrates have been reported, for examples by chemical vapor deposition of fluoroalkyl silane on a layer-by-layer assembled porous surface,[17] or by infusing a low surface energy liquid into the intrinsic pores of anodized alumina.[18] However, self-healing superamphiphobic fabrics have received little attention until very recently, when we reported the use of a fluorinated-decyl polyhedral oligomeric silsequioxane (FD-POSS) and fluoroalkyl silane (FAS) to develop the fabric coating.[20] However, the commercial unavailability of FD-POSS could be an issue limiting the wide use of this coating system in practices.

In our recent study, we have found a new coating system that can make fabrics have a durable self-healing superamphiphobic surface using a two-step wet-chemistry coating technique. The coating consists of a commonly-used, commercially-available fluoro-containing polymer, poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), a FAS, and a surface modified silica nanoparticle. In this paper, we report on this simple, but effective fabric coating, and its remarkable durability and self-healing performance. A plain weave polyester fabric was mainly used as the coating substrate.

2. Results and Discussion

The chemical structures of PVDF-HFP and FAS are shown in **Figure 1**a and the process to prepare the superamphiphobic fabric is schematically illustrated in Figure 1b. Two coating solutions, a nano particulate silica sol that was co-hydrolyzed from tetraethylorthosilicate (TEOS) and FAS in ethanol under an alkaline condition,[21] and a PVDF-HFP/dimethylformamide (DMF) solution containing FAS, were applied in sequence onto the fabric using a dip-coating method. The nanoparticles in the first coating solution had a concentration of 1.5 wt%, and they can be easily applied onto the fabric substrate through a dip-coating process. The average size of silica particles was around 150 nm with a standard deviation of 57 nm (see the scanning

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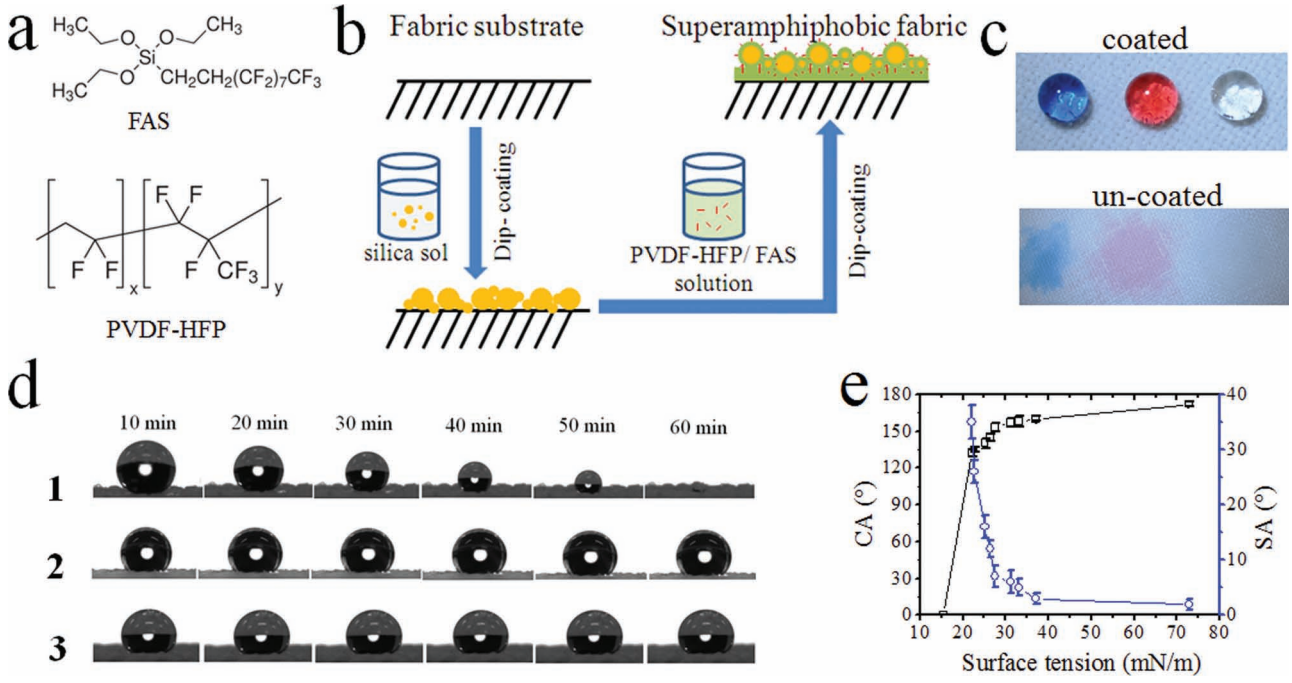

Figure 1. a) Chemical structure of FAS and PVDF-HFP. b) Coating procedure for superamphiphobic fabrics. c) Photograph of blue-colored water, red-colored hexadecane and clear soybean oil on the coated and un-coated polyester fabrics (10 μL for each drop; the small amount of dye used, oil blue in water and oil red in hexadecane, had no influence on the contact angles). d) Variation of liquid drops with time: 1) water, 2) soybean oil, and 3) hexadecane. e) Dependency of CA and SA on the surface tension of liquids.

electron microscopy (SEM) image and the size distribution histogram in the Supporting Information).

Figure 1c shows the super-repellency of the coated polyester fabric to liquid droplets (10 μL). Sphere-like droplets of blue-colored water, red-colored hexadecane and clear soybean oil were formed stably on the coated fabric. The coated fabric showed a contact angle (CA) of 172°, 165° and 160° to water, soybean oil and hexadecane, respectively. The sliding angle (SA) was used for measuring the contact angle hysteresis, which was 2°, 5° and 7°, respectively for water, soybean oil and hexadecane droplets.

To prove the stability of the liquid repellency, the liquid droplets were left on the coated fabric for an hour. As depicted in Figure 1d, the droplets do not reduce the CA during that time. The water droplet became smaller with time due to the evaporation of water from the droplet, while the oil fluids showed a very small change in size. After 60 min of leaving the droplets on the coated fabric led to an insignificant change in sliding angle (2°, 6° and 8° for water, soybean oil and hexadecane, respectively). The stable droplet with a small sliding angle indicated that the contact between the liquids and the coated fabric followed a Cassie-Baxter model.[22,23] For comparison, liquids were dropped on the uncoated fabric, which spread into the fabric completely because of the hydrophilic nature.

A series of organic solvents having different surface tensions have been used to explore the repellency of the coated fabric. The dependence of CA and SA on the surface tension of the liquids is shown in Figure 1e. It is clearly indicated that the coated fabric is super-repellent to both water and oil fluids with a surface tension larger 27.5 mN/m, a typical characteristic of superamphiphobicity.

To further prove the excellent repellency, the coated fabric was completely immersed in a liquid fluid, and then the wettability was observed. After 4 weeks of immersion in water, the coated fabric was still dry with the superamphiphobic feature maintained. This is because an air gap is formed between water and coated fabric. If the air layer was removed by a vacuum treatment, the coated fabric could be wetted and in this case water can wick into the fabric matrix. However, once the wetted fabric was dried at room temperature, the fabric became superamphiphobic again (Supporting Information). In comparison, oils were relatively easier to wick into the coated fabric when it was immersed into the oil fluid for a certain period of time. For soybean oil, complete wetting took about 12 h. However, once the fabric was rinsed with ethanol to clean the oil from the surface and then dried at room temperature, its superamphiphobicity was restored. For hexadecane, a shorter immersion time (5 h) was required to wet the fabric. Similarly, such a forced wetting state occurred only temporarily, and once the oil was cleaned from the surface, the superamphiphobicity reappeared (Supporting Information).

Figure 2a,b show SEM images of the coated and un-coated polyester. A particulate morphology can be clearly observed on the fiber surface after coating (Figure 2a), which provides roughness at the nanoscale to compliment the microscale roughness inherent in the fabric weave. The resulting hierarchical roughness on the nano- and microscales formed by the coated fabric are well known to enhance the liquid repellency. Using transmission electron microscopy (TEM), the

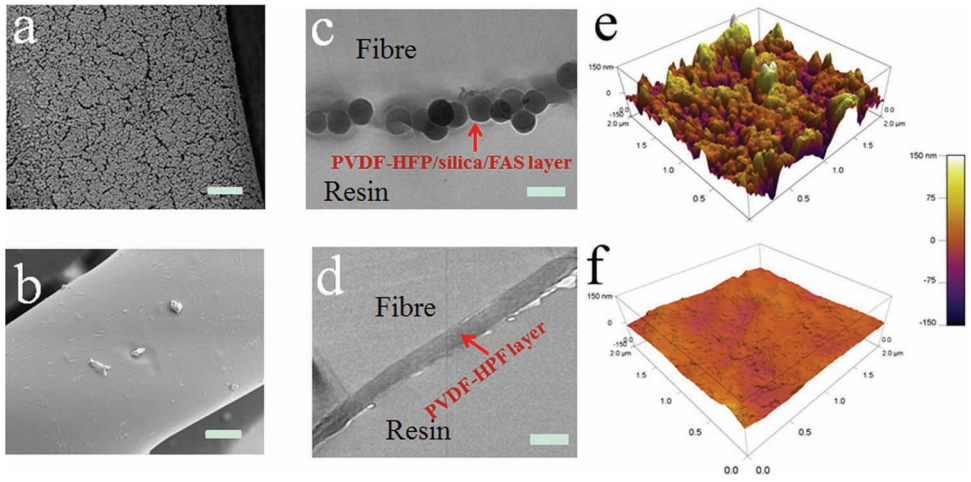

Figure 2. SEM images of polyester fiber a) coated and b) uncoated (scale bar = 2 μm). Cross-sectional TEM images of c) PVDF-HPF/FAS/silica nanoparticle coated polyester fiber and d) PVDF-HFP coated fiber (scale bar = 200 nm). AFM images of the polyester fibers: e) PVDF-HFP/FAS/silica nanoparticle coated fiber and f) uncoated fiber.

nanoparticle within the coating layer can be clearly identified. The coating thickness measured based on the TEM image was about 250 nm (Figure 2c). For comparison, the cross-sectional TEM image of the PVDF-HFP coating only (without silica nanoparticles) is shown in Figure 2d, which looks smoother with a thickness of 96 nm.

Images recorded using atomic force microscopy (AFM) also revealed the nanoscale roughness of the surface coating (Figure 2e,f). Based on the AFM images, the root mean square (RMS) roughness of the polyester fabric was measured. Without any coating treatment, the polyester fibers have a RMS roughness of 8.3 nm (Figure 2f), while the fibers after PVDF-HFP/nanoparticle coating have an RMS roughness of 46.0 nm (Figure 2e).

Washing and abrasion durability of the coated fabrics were evaluated. After 600 cycles of standard machine laundry, the coated fabric still maintained its superamphiphobicity. Both the CA and SA underwent a slight change with the washing cycles (**Figure 3**a,b). The 600 cycles of standard machine laundry without loss of the surface properties suggests that the coated fabric can maintain the superamphiphobicity for up to 11.5 years of uses if it is washed once a week and washing is the only cause to degrade the surface property. After 600 cycles of washing, silica particles can be clearly observed on the coating surface (see the SEM image in the Supporting Information), indicating that the particles are immobilized firmly on the fiber surface.

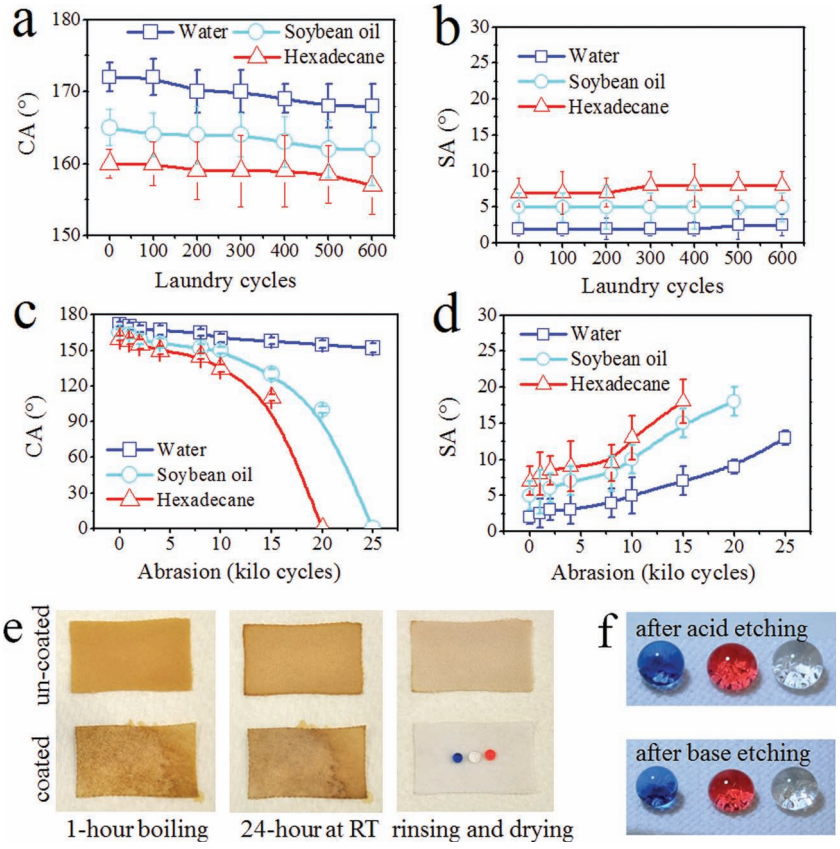

Figure 3. a) CA and b) SA change with laundry cycles. c) CA and d) SA change with abrasion cycles. e) Photographs of uncoated and coated polyester fabrics after being boiled in coffee, left at room temperature for 24 h, rinsed with water, and then dried at room temperature. f) Photographs of colored liquid droplets (blue water, red hexadecane and clear soybean oil, all in 10 μL) on the coated fabric after immersion in strong acid or base solution for 7 days (after acid etching CA: 170°, 163° and 160° for water, soybean oil and hexadecane, SA: 2°, 5° and 8° respectively; after base etching CA: 170°, 164° and 160°; SA: 2.5°, 5° and 7.5° for water, soybean and hexadecane, respectively).

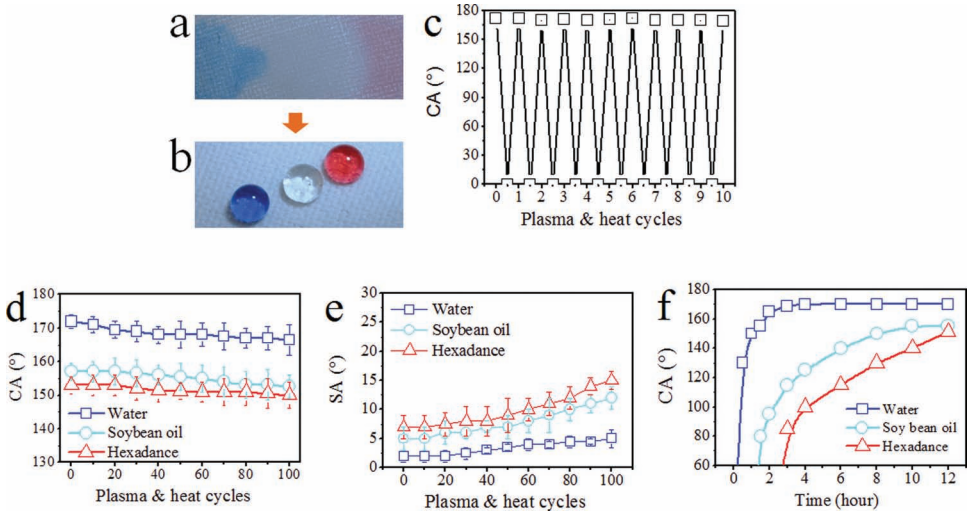

Figure 4. Photographs of colored liquids (blue-colored water, red-colored hexadecane and clear soybean oil) on a) the coated fabric after the first plasma treatment and b) the coated fabric after 100 cycles of plasma & heat treatments. c) Water CA change in the first 10 cycles of plasma-and-heat treatment. d) CA and e) SA change with the plasma-and-heat treatment cycles. f) CA changes with ageing time at room temperature (after 100 cycles of plasma-and-heat treatment).

The abrasion durability was tested using the Martindale method using untreated fabric to simulate actual wear. A load pressure of 12 kPa was employed, which is typically used for evaluating heavy duty upholstery usages. As shown in Figure 3c, after 8,00 cycles of abrasion, the coated fabric changed its CA to 165°, 152° and 145° respectively to water, soybean oil and hexadecane. Although the SA increased with increasing the abrasion cycles, it was still lower than 10° to all the liquids after the fabric was subjected to 8000 cycles of abrasion (Figure 3d). This result indicates that the coated fabric can withstand 8000 abrasion cycles without a significant reduction in its superamphiphobicity. After 25 000 abrasion cycles, the coated fabric still retained its superhydrophobicity, although it lost the oleophobicity. It was also found that the 25 000 cycles of abrasion led to the occurrence of physical damage to both the fibers and the fabric structure. It has been established that a fabric capable of withstanding 20 000 cycles of abrasion can be used commercially, therefore the superamphiphobicity of this coated fabric would last for roughly 32% of the fabrics expected lifetime.

The coating showed excellent stability against boiling treatment in aqueous solutions. After boiling in water for 1 h, the coated fabric showed no change in the superamphiphobicity (Supporting Information). When the coated fabric was boiled in coffee for 1 h and then left at room temperature for 24 h, followed by rinsing with water and finally drying at room temperature, the coated fabric was not stained at all and still maintained the super liquid-repellency (Figure 3e).

Apart from the boiling test, a standard procedure (AATCC method 175-2008, stain resistance: pile floor coverings) was employed to examine stain resistance using a natural cherry powder as the colorant. After 24 h of staining, the coated fabric was easily cleaned by rinsing with water (Supporting Information). Such an excellent stain resistance could be useful for antifouling of organic contaminants.

The coating was also very stable in strong acid and base solutions. After immersing the coated fabric in an aqueous H_2SO_4, HCl or HNO_3 solution (pH = 1), or an aqueous KOH solution (pH = 14) for 7 days, the coated fabric showed almost no change in its superamphiphobicity (Figure 3f). The SEM images of H_2SO_4 and KOH treated fabrics confirmed that no morphological change occurred to the coated fiber surface after the acid or base treatment (Supporting Information). In addition, the coated fabric was very stable in an ozone environment. After exposure of the coated fabric to air containing ozone (concentration, 6%) for 10 hours, the liquid repellency did not change (Supporting Information).

The self-healing ability of the superamphiphobic coating was investigated by artificially damaging the coated fabric with a vacuum plasma treatment using air as the gas source, which introduced oxygen-containing hydrophilic groups on the coating surface. After 5 minutes of plasma treatment, the coated fabric became both hydrophilic and oleophilic with a contact angle of 0° to water, soybean oil and hexadecane (**Figure 4**a). However, when the plasma treated fabric was heated at 130° for 5 min, it restored the superamphiphobicity with a contact angle of 171°, 165° and 160° to water, soybean oil and hexadecane, respectively (Figure 4b). This self-healing was repeatable and worked for many cycles. Figure 4c shows the change of CA in the first 10 cycles of plasma and heat treatments. With increasing the treatment cycles, the CA reduced slightly, but was still in the superhydrophobic range. Figure 4d,e show the CA and SA changes with the plasma-and-heat treatment cycles. The CA reduced while SA increased with the increase in the plasma-&-heat treatment cycles. It was interesting to note that the treated fabric retained its superamphiphobicity even after 100 cycles of the treatments, and after 100 cycles of plasma-and-heat treatment, the SA was still very low, being 5°, 12° and 15° for water, soybean and hexadecane, respectively (Figure 4e). Under SEM, the coated fabric surface after 100 cycles of plasma-and-heat treatments still showed the micro- and nanoscaled hierarchical structure (Supporting Information). In addition, the self-healing can also take place at room temperature. As shown in Figure 4f, the treated fabric at

Table 1. Influence of coating materials on surface wettability.

Coating materials			Properties of coated fabrics			
Hydrophobic silica	PVDF-HFP	FAS	Superhydrophobicity	Superoleophobicity	Self-healing	Durability
✓			Yes	No	No	No
✓	✓		Yes	No	No	Yes
✓		✓	Yes	No	No	No
	✓		No	No	No	No
	✓	✓	Yes	No	Yes	Yes
✓	✓	✓	Yes	Yes	Yes	Yes

room temperature slowly increased its contact angle to all three fluids tested after the plasma treatment, and within 12 h the surface returned to a superamphiphobic state.

The Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy was employed to examine the change of surface functionalities after plasma and heat treatments (Supporting Information). After the coating treatment of fabric, new peaks at 1200 cm^{-1} and 1150 cm^{-1} occurred, which were assigned to the C–F stretching vibration of the fluorinated alkyl chains. This was also accompanied by a considerable reduction in the peaks 1710, 1250 and 1120 cm^{-1}, respectively assigned to the carbonyl stretching band, CH_3 and CH_2 of the underlying polyester fabric. After plasma treatment, the C–F peaks at 1200 cm^{-1} and 1150 cm^{-1} reduced considerably, while the peak at 1100 cm^{-1}, which corresponded to C–O stretch vibration, increased. When the plasma treated fabric was heated, the C–F bonds recurred, as evidenced by the return of the corresponding peaks in the FTIR spectra. The same result was obtained by ageing the plasma treated fabric at room temperature for 12 h. This indicates that plasma treatment introduces oxygen and removes C–F bonds from the coating surface, while heating treatment or room temperature ageing leads to the re-emergence of the C–F bonds to the surface.

It should be noted that PVDF-HFP itself is hydrophobic in its own right, and applying PVDF-HFP alone to the fabric led to an increased water CA (Supporting Information). However, the PVDF-HFP coating reached a water CA of 140°. Increasing the PVDF-HFP thickness did not make the coated fabric superhydrophobic, but decreased the fabric permeability (Supporting Information).

To determine the role of each coating component in the superamphiphobic and self-healing functions, a series of control experiments were conducted, as listed in **Table 1**. When a thin layer of hydrophobic silica nanoparticles was applied onto fabrics, they showed strong superhydrophobicity, but had no self-healing property; the coating also had poor washing and abrasion resistances. When fabric was coated with hydrophobic silica nanoparticles and then a thin layer of PVDF-HFP, the fabric became superhydrophobic with much improved washing and abrasion durability; however, the coating was neither superoleophobic nor self-healable. When fabric was treated with PVDF-HFP solution alone, the coated fabric only had a water contact angle of 140°, with no oleophobicity. Adding FAS to the PVDF-HFP layer resulted in a superhydrophobic surface (CA = 156°) with self-healing ability, but it was still not oleophobic. When the silica nanoparticle coated fabric was coated with FAS, the oleophobicity was improved, but the fabric was still not superoleophobic.

These results suggested that the superoleophobicity was derived from a joint action of nanoparticles, PVDF-HFP and FAS. The silica particles assisted in forming a rough surface on the fibers, while the FAS and PVDF-HFP contributed to lowering the surface free energy. PVDF-HFP also functioned as a binding agent to immobilize the particles in the coating layer, hence improving the durability. The addition of FAS to PVDF-HFP renders the coating with the self-healing ability.

It should be noted that PVDF-HFP has a low glass transition temperature (T_g, –40 °C), making it a thermoplastic elastomer at room temperature. The addition of FAS to PVDF-HFP did not change the T_g (see the Supporting Information). The low T_g facilitated the movement of FAS molecules in the coating layer.

The mechanism for self-healing of a surface property has been proposed by a few groups.[17,24] In our case, the mechanism likely follows the steps outlined here: When the coating surface was damaged chemically (e.g., plasma treatment), polar groups were introduced to the surface, leading to reduced amphiphobicity because of the increased surface free energy. Since the coating has a low T_g, the mobility of molecular migration and movement in the coating layer is high. The tendency to minimize the surface free energy is the driving force behind the fluorinated alkyl chains migrating toward the coating surface. As a result of covering the polar groups with the fluorinated alkyl chains, the surface free energy decreased considerably, resulting in recovery of superamphiphobicity. This molecular migration can be typically sped up by increasing the temperature, which increases the self-healing speed.

Besides polyester fabric, other types of fabrics, such as cotton and wool fabrics had also been used as substrate. The treated fabric always showed durable superamphiphobicity and self-healing ability (Supporting Information). The coating treatment showed very little influence on the air permeability of the fabric, and washing, abrasion, acid/base etching and boiling treatment also showed almost no influence on the permeability as well (Supporting Information).

3. Conclusion

In summary, a robust, superamphiphobic fabric having a novel self-healing ability to auto-repair against chemical damages can be prepared by a two-step coating technique using easily

available materials. This simple and effective coating system may be useful for development of robust protective clothing for various applications.

4. Experimental Section

Materials: 1H,1H,2H,2H-perfluorodecyltriethoxysilane ($C_{16}H_{19}F_{17}O_3Si$) supplied by Sigma, and poly(vinylidene fluoride-*co*-hexafluoropropylene) (Mw = 470,000, polydispersity = 3.2), dimethylformamide, tetraethylorthosilicate (98%), ammonium hydroxide (28% in water), oil red and oil blue obtained from Aldrich were used as received. Commercial polyester fabrics (plain weave, 168 g/m^2, thickness = 520 μm), cotton fabric (plain weave, 160 g/m^2, thickness = 520 μm) and wool fabric (plain weave, 196 g/m^2, thickness = 530 μm) were purchased from local supermarket, and they were rinsed with acetone and distilled water and cut to 5 cm × 5 cm (each sample) before use.

Silica particulate solution was prepared according to our previously reported method with a slight modification. Briefly, ammonia (4 mL) and ethanol (50 mL) were mixed to form a homogenous solution, and TEOS (4.5 mL) was then added. After 2 h of magnetic stirring, 0.25 mL FAS was added to the reaction solution. The reaction was allowed to stir for another 1 h at room temperature to form a hydrophobic silica particulate sol. Under this synthesis condition, the silica particles had a concentration of 1.5 wt% in the solution.

PVDF-HFP/FAS solution was prepared by mixing PVDF-HFP (1.0 g) and FAS (0.5 mL) in DMF (50 mL) to form a homogenous solution. After 0.5 h of magnetic stirring, the solution was ready for coating on fabrics.

Fabric Coating: A two-step dip-coating method was used to treat fabrics. In the first step, the fabric substrate was immersed in the silica particulate solution (silica particle concentration, 1.5 wt%) for 1 min to apply silica nanoparticles to the fabric surface. The treated fabric was then dried at room temperature for 10 min. Without any rinsing, the particle-coated fabric was immersed in the second coating solution for 1 miute to apply PVDF-HFP/FAS on the surface. The coated fabric was finally dried at 130 °C for 1 h.

Plasma Treatment: The coated fabrics were subjected to a vacuum plasma treatment using a purpose made plasma machine consisting of a vacuum chamber, a radio-frequent plasma generator (T & C Power Conversion, Inc. AG0201HV), an electrode system, and a gas supplying system. For each plasma treatment, 5 min of plasma treatment under a power of 19 W was employed. Such a plasma treatment can make fabrics completely hydrophilic and oleophilic (CA = 0°). The plasma treated fabric was then heated at 130 °C. The self-healing was also performed by ageing the plasma treated fabrics at room temperature. All the plasma treatment used the same operating parameters in this study.

Acid and Base Stability Tests: The coated fabric was immersed in strong acid (H_2SO_4, HNO_3, or HCl) (pH = 1) or KOH solution (pH = 14) at room temperature for 7 days. The immersed fabric was then rinsed with water and dried at room temperature for 30 min.

Washing Durability Test: The washing durability was evaluated by reference of the washing procedure described in the AATCC (American Association of Textile Chemists and Colorists) Test Method 61-2006 test No. 2A. The test was performed using a standard laundering machine (Fong, Fong's National Engineering CO.LTD, Hong Kong, China) equipped with 500 mL (75 mm × 75 mm) stainless-steel lever-lock canisters. The fabric sample (size, 50 mm × 150 mm) was laundered in a 150 mL aqueous solution containing 0.15% (w/w) AATCC standard reference detergent WOB and 50 stainless steel balls. During laundering, the temperature was controlled at 49 °C, and the stirring speed was 40 ± 2 rpm. After 45 min of laundering, the laundered sample was rinsed with tap water, and then dried at room temperature without spinning. The contact angle and sliding angle were then measured. This standard washing procedure is equivalent to five cycles of home machine launderings. For convenience, we used equivalent number of home laundering in this work.

Abrasion Resistance Test: The abrasion resistance was tested using the Martindale method according to ASTM D4966. The test was performed under a commercial Martindale abrasion tester (I.D.M Instrument Design & Maintenance). In our experiment, the untreated fabric was used as the abradant. 12 kPa of pressure was employed, which is often used to evaluate the coated fabrics for heavy duty upholstery usages.

Boiling in Coffee Solution: Fabric was soaked and boiled in coffee (Moak, 5 g 100% pure soluble coffee powder added in 150 mL boiling water) solution for 1 h. The fabrics were allowed to stay undisturbed for 24 h. The stained fabrics were then rinsed thoroughly with cold tap water and dried at room temperature.

Staining with Mixed Cherry Solution: The stain resistance was also tested using a modified procedure based on the AATCC Test Method 175-2008 (Stain Resistance: Pile Floor Coverings). In brief, a cup of standard cherry-flavored, sugar-sweetened, Kool-Aid Brand powdered drink mixed solution was poured onto the top surface of the coated fabric and the staining solution was mechanically worked by hand to obtain uniform staining. The fabric was then left to stand undisturbed for 24 h. The stained fabric was then rinsed thoroughly with cold tap water and dried at room temperature.

Ozone Oxidation: Ozone was generated by an ozone generator (Catalytic Ozone Destruct IBC 7430, USA) through feeding 1 L/min air into the generator at room temperature. Under these conditions, the generator could produce 6% ozone in air. The coated fabric was mounted on the large end of a funnel. Ozone/air was fed from the other funnel end at room temperature.

Other Characterizations: SEM images were taken using an SEM Supra 55VP operated at an acceleration voltage of 5.0 kV. AFM (Asylum Research) was used to measure surface roughness. TEM (JEM-200 CX JEOL, Seike Instrument) was used to observe the coated films. CA measurements were carried out on a contact angle goniometer (KSV CAM 101) using liquid droplets of 5 μL in volume. The diameter and distribution of silica particles were measured by a particle sizer (Zeta Sizer, Nano series). Air permeability was examined by FX 3300 Air permeability Tester according to the Standard (SIST EN ISO 9237-1999). All the CA and air permeability values reported represent the mean of 5 measurements. FTIR spectra were recorded on a Bruker VERTEX 70 instrument in ATR mode at a resolution of 4 cm^{-1} accumulating 32 scans. Differential scanning calorimetry (DSC) measurements were conducted by using DSC Q 200 (TA Instruments) under nitrogen. Samples of about 5–10 mg were enclosed in aluminum DSC capsules, and heated from –50° to 250° at a rate of 10 °C/min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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