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A novel strategy for fabricating robust superhydrophobic fabrics by environmentally-friendly enzyme etching

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Abstract

Superhydrophobic silk fabrics were prepared using an environmentally friendly enzyme-etching approach, followed by the modification with methyltrichlorosilane (MTCS) via a simple thermal chemical vapor deposition (CVD) process at 70 °C. The effects of the concentration, treatment time and temperature of enzyme on the etched surface properties were discussed. The composite superhydrophobic silk fabrics demonstrated excellent self-cleaning ability, relatively unscathed effecting their intrinsic properties such as the luster, softness, color and style of the fabrics. Furthermore, these treated fabrics demonstrated excellent mechanical durability after silane-treatment as evidenced by the cyclic abrasion and laundering tests. The composite superhydrophobic

cotton fabrics have also demonstrated a high efficiency in oil-water separation. The facile technology via enzymatic hydrolysis to etch the substrate possesses extensive potential applications on various other cellulose-based substrates.

Keyword: superhydrophobic, fabrics, fluorine-free, enzyme etching, self-cleaning, oil/water separation

1. Introduction

Inspired by lotus leaf, water striders and nepenthes, superhydrophobic surfaces with a high water contact angle (CA) and low sliding angle (SA) have received intensive attention in recent research.[1-5] Numerous promising applications have been proven, including self-cleaning, oil-water separation, water collection, anti-fogging/frosting, drag reduction, energy conversion, stimuli-responsive, droplet manipulation, and electronic device protection.[6-10] The study of superhydrophobicity has also been extended to include multiple functional performances, including UV-resistance, shape memory, and thermal isolation and so on.[11-13]

Textiles are of great interest as substrates because of their flexibility and high specific surface areas, especially the abundance, easy production, and environmental friendliness of the raw materials.[14] They have a micron-sized structure, and the diameter of a single fiber is micron or even nanometer. A micro-nanostructure surface can be easily obtained by this natural advantage combined with a simple further processing, which can provide a very favorable condition for the formation of superhydrophobic interface. Among numerous types of textiles, the one by silk, a natural protein fiber, enjoys excellent properties such as elegant appearance,

softness, luster, warmth, biodegradability, skin-friendliness, renewability, moisture management, and overhanging performance, endowing it the best quality fabric among different types of textiles.[15, 16] With its rapid expansion in applications, silk fabric has extended from its conventional light summer clothing material into multi-functional, for example, superhydrophobic, breathable suit, ski jacket, high-grade trench coat, interior decoration for cold season wear. One of the obstacles for the extended application lies with the fact that there are abundant hydrophilic groups, such as hydroxyl, carboxyl, and amino groups, on the surface of silk fibers.[17]

It is well known that the hierarchical micro-/nanostructures and low surface energy materials are two pivotal factors for the construction of superhydrophobic interface.[18, 19] Representative bottom-up approaches to prepare superhydrophobic surfaces involve dip-coating, chemical bath deposition, atomic layer deposition (ALD), atom transfer radical polymerization (ATRP), electrostatic layer by layer self-assembly, *in situ* growth, wetting chemical coating, chemical vapor-phase deposition, polymer grafting, *etc.*[18, 20-27] Of all the research techniques, fluoride decoration is frequently used because fluorine is the most electronegative element so that the forces between the perfluorocarbon chains are weak and the surface tension of fluorine-decorated surface is much reduced.[28, 29] Some fluorinated hydrophobic coating, such as fluoroalkylsilane (FAS)-modified SiO₂ nanoparticles and perfluorodecyltriethoxysilane (PFTS)-treated TiO₂ and SiO₂ nanoparticles have been used to improve the hydrophobicity.[30, 31] However, the fluorinated coating are limited due to their environmental persistence, toxic potential and high price. Therefore, environmentally friendly new methods of fluorine-free hydrophobic finishing strategies need to be developed. Moreover,

hydrophobic treatment of silk fabrics is limited by certain inherent deficiencies of the fiber surface, such as lack of the required surface micro/nano features, low thermal stability, and tendency to be discolored with organic solvents, which has put stringent limitations on the decoration processing conditions. Among some past efforts, Xu *et al.* successfully constructed hydrophobic silk fabrics, by ALD coating of TiO₂ particles to realize a hierarchical rough structure.[32] However, the preparation process is complicated and the hydrophobic effect is limited. There are also other methods, such as plasma etching, dip-coating, hydrophobic finishing and ATRP to generate roughness on silk fabrics and reduce surface energy.[33-36] However, these approaches require either stringent experimental equipment, or high reaction temperature and/or use of organic solvents, which are not appropriate for silk fabrics for reasons mentioned above. It is extremely difficult to construct a rough texture on the surface of smooth silk without affecting its physical and mechanical properties. Therefore, novel and environmentally friendly techniques towards functional superhydrophobic textiles are highly in demand.

Enzymes are generally used as a catalyst because of their excellent activity, easy degradation and high selectivity. Among different types of enzymes, papain has a high enzyme activity, good thermal stability, is safe to human health, and has been used for silk degumming.[37-39] Mi *et al.* reported a nanochannel reactor using the gas-solid-liquid interfaces with controlled wettability to boost the catalytic efficiency of glucose oxidase.[40] Enzymes not only can play a role in catalysis, but also can be used to hydrolyze amino acids.[41] Papain is a kind of protease that can degrade proteins in acidic, neutral, and alkaline environments without adding particles or using special instrument. Therefore, it will be an advantage to use enzyme to etch silk fibers by a

simple dipping action, which is both convenient and environmentally friendly. Furthermore, the principle of enzymatic hydrolysis is applicable for etching various types of other substrates.[42] For example, esterase, can be used for the etching of polyester fabrics.[43] However, that being able to generate rough surface does not always lead to superhydrophobic surface, low surface energy is also needed. In this regard, hydrophilic groups on silk fabric surfaces can be used to graft low surface energy compounds.[44] For example, methyltrichlorosilane (MTCS) can reduce the surface energy of the substrate because of its methyl group, and has a low boiling point of only 66 °C, while other low boiling silane can also be used by a low temperature CVD process.[45, 46] This method of using enzyme etching, followed by MTCS decoration, can prevent the silk fabric from being discolored by organic solvent, and avoid reliance on high temperature during processing.

2. Experimental Section

2.1. Materials and reagents

Papain, Alkaline protease, Cellulose, triethoxyoctylsilane and methyltrichlorosilane (MTCS) were purchased from Sigma-Aldrich and used without further purification. Silk, wool and cotton fabrics were purchased from a local fabric store. They were ultrasonically cleaned with ethanol and deionized water to remove possible contamination.

2.2. Preparation of surface roughness

Papain (2.5 g) was dissolved in 250 mL of deionized water and stirred at ambient temperature until the papain was completely dissolved. Then, the cleaned silk fabric (4

cm × 4 cm) was immersed in the papain solution (10 g L⁻¹), and then placed in a Water-bathing Constant Temperature Vibrator at 70 °C for 30 minutes. The ratio of fabric to water was 1:100 and the pH value was controlled to be 7. The influence of the concentration, treatment time and temperature of enzyme on the surface morphology and hydrophobicity of the enzyme-etched fabrics was investigated.

2.3. Preparation of superhydrophobic silk fabrics

Deionized water was used to wash the treated silk fabric twice and dried at 80 °C. Subsequently, the above-mentioned silk fabric was hung over a Teflon-lined stainless steel vessel which contains 1 mL of MTCS by a wire, which prevented the fabric from contacting the organic solvent directly. And then the reactor was placed in a 66 °C oven for 10 hours, finally the superhydrophobic silk fabric was obtained. The super-hydrophobic fabric prepared by this method was called “standard sample”.

2.4. Characterization

The morphology of the treated silk fabric was examined using a field emission scanning electron microscope (FESEM, Hitachi S-4800) at 3.0 kV. An energy dispersive X-ray spectrometer (EDS) attached to the FESEM was used for chemical composition analysis. Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 5700 instrument. The wetting properties of deionized water on the treated silk fabric was measured using a Krüss DSA 100 (Krüss Company, Germany) apparatus. The volumes of droplets used for static contact angle and sliding angle measurements were 6 µL and 10 µL, respectively. Average water contact angle was obtained by measuring the same sample at three different positions. Surface roughness was tested using an atomic force microscope (AFM, Dimension Loon, Bruker Company). Tensile strength and elongation

at break were obtained by using a universal testing machine INSTRON-3365. The washing durability of as-obtained samples was evaluated according to the standard AATCC 61-2006 method under 2A condition. In the abrasion test, a pristine silk fabric was used as the abrasion surface, while the superhydrophobic fabric was tested facing this abrasive material. In addition, the permeability, bending modulus, and white index were measured, respectively, using a digital air permeability measuring instrument (YG461E-11), a fabric style instrument (KESFBAUTO-A), and a spectrophotometric color measuring instrument (DATACOLOR 600).

3. Results and discussion

As shown in Fig. 1a, the surface of pristine silk fabric is very smooth without micro/nano-structures. After treated with environmentally friendly and easily degradable papain solution (Scheme 1), a uniform grooved structure appeared on the surface of silk fabric (Fig. 1b). We adopted papain that was originally used as a degumming treatment for silk to construct the rough structure. After the enzyme-etching, the fabric surface became roughness, rugged and the silk fibroin was partially dissolved to form a block-like shedding so that the trenches on surface of fabric were constituted. This verified that they were caused by the erosion effect of papain on the surface of silk fibroin. A uniform coating covered with compounds on the silk fabric surface can be observed, after the MTCS treatment by CVD (Fig. 1c). Silicon and chlorine mapping images showed in Fig. 1d confirms that the silane was uniformly grafted on the MTCS@enzyme-etched fabric. The elements on the whole MTCS@enzyme-etched fabric surface were mainly C, O, S, Si, Cl and Pt. While the pristine silk mostly consists

of C, O and S elements. The presence of Pt element is due to the thin platinum coating on the etched sample for SEM observation. After silanization, the EDS displayed that the relative atomic percentage of silicon element is 4.69 (Fig. 1e).

Figure 1. SEM images of pristine silk fabric (a), papain-etching silk fabric (b) and MTCS@papain-etched silk fabric (c). Element mapping (d) and EDS (e) of MTCS@papain-etched silk fabric. Insets of (a), (b) and (c) are the corresponding high-magnification images.

Scheme 1. Schematic illustration of the procedure used to construct fluorine-free fabrics with special wettability: superhydrophilic pristine fabric, superhydrophilic enzyme-etching robust fabric, and robust and environmentally friendly superhydrophobic MTCS@enzyme-etching fabric.

To investigate the surface structure change caused by enzyme treatment, atomic force microscopy (AFM) was employed to characterize the surface roughness. The pristine silk fabric is extremely smooth with a root mean square (RMS) value of about 1-5 nm (Fig. 2a). The roughness increased to 30-35 nm after papain-etching (Fig. 2b) and a clear surface morphology change was observed. The roughness further increased to 86-91 nm on silk fabric after modified with MTCS. The initial enhanced RMS was resulted from the grooved structure of silk fabric surface with enzyme-etching. The further increase of RMS value is due to the self-assembly of methyltrichlorosilane on the surface of the enzyme-etched fabric.

Figure 2. AFM images of the surface of pristine silk fabric (a), papain-etching silk fabric (b), and MTCS@enzyme-etched silk fabric (c).

The surface chemical compositions of silk fabric before and after treated with papain and MTCS were investigated by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). As exhibited in Fig. 3a, the absorption bands at $\sim 780 \text{ cm}^{-1}$ and $\sim 1272 \text{ cm}^{-1}$ are ascribed to the characteristic vibrations of O–Si–O and C–Si asymmetric stretching in C–Si–O units, respectively.[47] This confirms the successful silanization in the MTCS@enzyme-etched silk fabric. As shown in Fig. 3b, the XPS survey spectra manifest that the main surface elements of pure silk sample and

papain-etching silk fabric were carbon and oxygen. This is due to the treatment of the silk fabric by papain is a kind of physical process, which did not change the surface chemical composition of the sample. After grafted with MTCS, two new peaks appeared at 101.0 eV and 152.0 eV corresponding to Si 2p and Si 2s, respectively, indicating that papain-etched silk fabric has reacted with MTCS (Fig. 3b and c). The high resolution O 1s spectrum displays two distinct peaks at 531.2 eV of the C=O bonds, and 532.6 eV of C–O bonds for blank sample (Fig. 3d). In addition, there was no change observed in the results of XPS spectra after enzymatic etching (Fig. 3e). However, the presence of strong Si–O peak (531.9 eV) indicates that MTCS binds with substrate through chemical bonding (Fig. 3f).

Figure 3. FTIR (a) and wide XPS (b) spectra and the high resolution Si 2p (c) spectrum of pristine silk fabric and silk fabric etched by papain and MTCS modification. High resolution for O 1s spectrum of pristine silk (d), papain-etching fabric (e) and MTCS@papain-etched fabric (f), respectively.

In the previous research on superhydrophobic silk fabric, the sample treated with organic solvents was found to turn slightly yellow. In this work, there was no significant

change in color according to optical photos of the fabric surface before and after the treatment (Insets of Fig. 4a). The measured white index of the fabric showed a slight decline (Fig. 4a) beyond detection by human eyes. Different kinds of color patterned fabrics were also employed as substrates (Fig. 4e-j). The images showed that there was no obvious change in color for the superhydrophobically modified fabric. This is accredited to our process that involved no organic solvents. The water contact angle of pristine silk fabric is almost 0° , but part of the silk fibroin was removed from the surface of fabric and hydrolyzed after being etched by papain. A further treatment by the grafting of MTCS achieves the increase of static contact angle. The MTCS@papain-etched fabric becomes superhydrophobic with contact angle of 153.5° and sliding angle of 8.5° . The transition from superhydrophilic to superhydrophobic is due to the enzyme-etching and the decoration of MTCS which has methyl groups with low surface energy and further increases in the surface roughness. However, the silk fabrics treated by MTCS can only achieve hydrophobicity and the contact angle of MTCS@silk fabric is 110° , which proved the importance of enzyme-etching.

Figure 4. White Index Commission Internationale de L'Eclairage (WI CIE) of fabric (a). [Abbreviation: PSF: pristine silk fabric, PSFH₀: papain-etching silk fabric, PSFH₃: papain-etching silk fabric treated with MTCS for 3 h, PSFH₅: papain-etching silk fabric treated with MTCS for 5 h, PSFH₈: papain-etching silk fabric treated with MTCS for 8 h, PSFH₁₀: papain-etching silk fabric treated with MTCS for 10 h.]. Insets of (a) are the corresponding optical photos of pristine silk fabric, papain-etching silk fabric and MTCS@papain-etched silk fabric, respectively. (b), (c), (d) are the static contact angles of pristine silk fabric, MTCS@silk fabric and MTCS@papain-etched silk fabric, respectively. (e), (g), (i) and (f), (h), (j) are the pictures of wettability of colored silk fabrics that are treated before and after.

The mechanism of enzyme-etching is the hydrolysis of fabrics via enzyme, such as protease which can be used to etch the biomass substrate. Papain was used to treat silk fabric to obtain rough surface texture in this study, and other proteases can also be used to hydrolyze silk fabrics. To confirm this, we used another protease to treat silk fabrics and endowed with superhydrophobic properties too. Fig. 5a showed the surface morphology after alkaline protease etched silk fabric, and the treated fabric obtained a contact angle of 156.7°. In order to further prove the mechanism of enzyme-etching, we also treated the wool fabric with alkaline protease, the results revealed that superhydrophobic wool fabric with contact angle of 152.3° has been successfully prepared (Fig. 5b). It can be attributed to the partly hydrolysis of the fabrics in the presence of alkaline protease. This system can also be used to treat other substrates with specific enzyme, such as cellulose enzymes can be used to deal with cotton, linen and other cellulose-based derivatives structures. The surface morphology and contact angle of cotton fabric treated by cellulose and MTCS is demonstrated in Fig. 5c. MTCS can also be replaced by other silane with a low boiling point. Fig. S1 showed the surface morphology of cellulose-etching cotton treated by triethoxyoctylsilane at 90 °C and the CA is approximately 153.0°.

Figure 5. SEM images of MTCS@alkaline protease-etched silk fabric (a), MTCS@alkaline protease-etched wool fabric (b) and MTCS@cellulase-etched cotton fabric (c). Insets of (a), (b) and (c) are the corresponding static contact angle images.

In addition, the temperature, concentration and reacting time of the enzyme will affect the surface roughness of the silk fabric. And when the surface roughness exceeds to a certain value, the wetting state would switch from “Wenzel” to “Cassie-Baxter”.[48] The specific impact of these factors on the roughness is further discussed next. Fig. 6 exhibits change in contact angle after grafting MTCS by CVD under different enzyme treatment conditions. The changes of contact angle on the enzyme-etched silk fabric is due to the variation in roughness. As shown in Fig. 6a, the fabric surface with the concentration of 10 g/L of enzyme-etching revealed a highest water contact angle of 155.5° among the different concentrations. It can be seen from the SEM that the wrinkles on the silk fabric surface with this concentration has the highest density (Fig. S2). The same trend between wetting state and morphology was observed for the surface etched under different reacting time and temperature (Fig. 6b, c and Fig. S3, S4). The highest contact angles of 155.9° was obtained after 30 minutes and 50°C in the respective studies. However, the temperature will affect enzyme activity resulting in the difference of roughness and silk fabric strength. The activity of the enzyme will increase with the temperature, but the activity of that will decrease if the temperature exceeds optimum

value. Therefore, considering the adverse effects on fabric strength, we chose 70 °C with a relatively high CA of 155.5° as the optimal parameter.

Figure 6. The effect of different concentration (a), time (b), and temperature (c) of the enzyme on contact angle.

To compare the self-cleaning performance of the pristine silk fabric, enzyme-etched fabric, and MTCS@enzyme-etched fabric, ground coffee powder was used as a model contaminant (Fig. 7). The coffee powder was spread on the surface of the fabrics, and subsequently washed with water jetting. Only the MTCS@enzyme-etched fabric demonstrated good self-cleaning ability, on which water droplets could easily roll down and took away the coffee powder along with them because of the extremely low water adhesion. The untreated fabric was completely wetted and the contaminant particles were left on the surface, while the contaminant was not able to infiltrate through the enzyme-etched fabric and MTCS@fabric due to their hydrophobic nature, but the surface was tarnished by the coffee powder.

Figure 7. Self-cleaning performance of different samples: groups A, B and C are samples of untreated, contaminated and water cleaned for pristine silk fabric, enzyme-etched fabric, and MTCS@enzyme-etched fabric.

The as-constructed cotton fabric demonstrated superhydrophobicity and superoleophilicity, and could be used as a selective filter to allow only oil to pass through. As shown in Fig. 8a–c, the treated fabric was placed between two glass tubes to be used as a filter membrane for oil-water separation. 100 mL of oil (dyed with dichloromethane with red color) and 100 mL of water (dyed with methylene blue) were mixed and then poured onto the superhydrophobic fabric membrane. Because of the immiscibility of oil and water, the mixture was quickly layered (Fig. 8a). Fig. 8c demonstrated the highly selective removal of oil from the layers due to the rapid and efficient oil clean-up (Movie S1). The separation efficiency was calculated based on the amount of collected product of water. As shown in Fig. 8d, all of the water was collected in the flask and original water as well as original oil was obtained, respectively, which shows a very high separation efficiency of the coated silk textile. After the tested sample was dried, the same filtering

process was repeated for 5 times without losing the oil-water separation performance.

Figure 8. Time sequence of the oil-water separation process with modified cotton fabric (a–c); the volume of water and dichloromethane before (d) and after (e) separation. There is a loss in the oil after filtration due to its volatility.

The CA variation on the MTCS@papain-etched fabric surface with number of abrasion cycles is shown in Fig. 9a. Obviously, the MTCS@papain-etched fabric surface remained highly hydrophobic after 150 cycles of abrasion using pristine silk fabric as abramer. The CA of water droplets placed on the fabric surface varied from 156.7° in the initial condition to 153.6° after 100 abrasion cycles, while the SA was from 8.5° to 15.6° (Inset of Fig. 9a). Although the anti-wetting property was gradually reduced with the increase of abrasion cycles, the CA remained at a high level after 150 cycles of abrasion. It was found that the rough surface texture of the MTCS@papain-etched fabric was retained after being repeatedly abraded (Fig. 9c–f). This enhanced mechanical resistance is due to the rough surface texture prepared by chemical etching which is more durable than physical coating.

Besides, washing durability is also essential for fabrics due to the requirement of

regular washing. The accelerated laundering durability test of treated silk fabric is performed according to the AATCC 61-2006 standard method under 2A conditions, and one cycle of accelerated laundering is equal to five cycles of domestic laundering. Fig. 9b showed that the prepared silk fabric remains superhydrophobic after 2 cycles of laundering with a CA of 150°. Consequently, the surface liquid repellency was reduced more drastically after 9 laundering cycles, the surface morphology suffers severe damage after 5 cycles of washing (Fig. 9g and h), which might be resulted from the effect of alkaline substances in soap on grafted silane of fabric surface.

Figure 9. The effect of abrasion and accelerated laundering times according to the AATCC standard method under 2A conditions on contact angle (a and b), insets of (a) are the corresponding SA and morphology (c–f) of the treated fabric after 0, 100, 200 and 250 abrasion cycles; (g) and (h) show fabric after 5 and 10 laundering cycles. Inset images of (c–h) are pictures of the droplet on the corresponding sample.

Apart from the physical durability assessment, we also evaluated the chemical stability of the superhydrophobic coating by measuring the changes of the CA after dripping drops of acid, alkali and salt solution on the surface of substrates, as well as immersing the fabric in highly concentrated acidic and basic solutions. The drops of acid, alkali and salt solutions on the surface of silk, cotton and wool fabric were shown in Fig. 10a-c, respectively. There was no drastic change in the contact angle of these drops (HCl, NaCl and NaOH with pH of 2, 7 and 12). However, after immersing the fabric in highly concentrated acidic and basic solutions (HCl and NaOH with pH of 2 and 12) for 24 hours, the water contact angle of silk fabric displayed a change as shown in Fig. 10d. The silk fabric is more vulnerable to strongly acidic solution and the WCA decreased to 132.5° after soaking in HCl solution for 24 h. The cotton fabric is not resistant to alkaline solution, and the WCA of wool fabric is kept at a high level under both conditions. Some morphological changes were observed on the fabrics surface tested in strongly acidic or alkaline solutions (Fig. S5). Some fraction of the coating was peeled off, resulting in a smooth surface in the part of fiber without any hierarchical structure. Overall, the groove structure etched by enzyme remains on fibers.

Figure 10. The drops of acid, alkali and salt solutions on the surface of silk (a), cotton (b) and wool

fabric (c), respectively. Contact angle of fabrics derived from different substrate after immersion into HCl solution (pH = 2) solution and NaOH solution (pH = 12) for 24 h.

Subsequently, we investigated the effect of enzyme-etching on the mechanical properties of textile fabric. The results of the tensile strength and elongation at break among the pristine, papain-etched fabric and MTCS@papain-etched fabric were summarized in Table 1. The extent of hydrolysis of papain on silk fibroin was very low, but the tensile strength of silk fibroin decreased after the enzyme etching. The loss of silk fibroin increased with the increasing of treatment time and concentration of enzyme, but it increased firstly and then decreased as the temperature increased. In addition, the bending modulus and air permeability of enzyme-etching fabric increased a little compared with that of pristine silk, which is attributed to the surface damage of fabric. The slight decrease of both of them resulted from the coating of saline.

Table 1 Physical properties of pristine silk fabric, papain-etching silk fabric and MTCS@papain-etched silk fabric.

Property	Pristine	Papain-etching	MTCS@papain-etching
Tensile strength (N cm ⁻¹)	546.07±30 (warp)	450.73±40 (warp)	408.23±39(warp)
	445.06±50 (weft)	385.01±36 (weft)	385.01±36 (weft)
Elongation at break (%)	26.63±1.71 (warp)	23.06±1.26 (warp)	23.06±1.26 (warp)
	14.32±1.79 (weft)	7.24±1.01 (weft)	7.24±1.01 (weft)
Bending modulus (gf cm ² cm ⁻¹)	0.0652 (warp)	0.0786 (warp)	0.0635 (warp)
	0.0146 (weft)	0.0208 (weft)	0.0143 (weft)
Air permeability (mm s ⁻¹)	116.05±5	120.96±6	108.24±4
White index (WI)	68.75	64.26	42.78

4. Conclusion

In this study, we have successfully constructed superhydrophobic fabric via an environmentally friendly strategy by etching the silk fabric using enzyme, and subsequently modifying it with MTCS by CVD. Three important parameters (concentration, temperature, reaction time) of enzyme treatment have been studied on their influence of the groove formation on silk fabric surface. It was found that the density and depth of the surface groove affect the surface roughness of the silk fabric and reduce its strength to some extent. By optimizing the experimental parameter, we prepared the superhydrophobic MTCS@enzyme-etched surface with a water contact angle of 156.7° and sliding angle of 8.5° , while minimizing the damage of physical and mechanical properties. The as-prepared MTCS@enzyme-etched fabric demonstrated good laundering and abrasion durability after repeated cycles. The MTCS@enzyme-etched fabric with special wettability has also been demonstrated for its effective self-cleaning and oil/water separation properties. In particular, the fluorine-free coating is environmentally-friendly, low-cost, and has no adverse effect on the important textile physical properties, such as air permeability and white index.

Furthermore, except for etching silk fabrics, other biomass substrates can also be used to etched by enzymes that can hydrolyze proteins. For example, alkaline protease can etch both silk fabrics and wool fabrics, which proves the versatility of this strategy. The system can be applied to other enzymes and substrates utilizing the specific character of enzyme. This facile process using enzymatic hydrolysis to etch substrates has extensive potential applications on various biomass substrates, which opens up a new avenue for the preparation of superhydrophobic surfaces.

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Supporting information

A novel strategy for fabricating robust superhydrophobic fabrics by environmentally-friendly enzyme etching

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Supplemental figure captions:

Figure S1. The surface topography of enzyme-etched cotton fabric treated by triethoxyoctylsilane at 90 °C.

Figure S2. The effect of different concentrations (0-30 g/L) (a-g) of the enzyme on surface morphology.

Figure S3. The effect of different treatment times (0-120 min) (a-e) of the enzyme on surface morphology.

Figure S4. The effect of different treatment temperatures (40-90 °C) (a-f) of the enzyme on surface morphology.

Figure S5. SEM and CA images of fabrics after immersed into hydrochloric acid solution (pH = 2) and sodium hydroxide solution (pH = 12) after 24 h for cotton (a, d), silk (b, e) and wool (c, f).

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Video

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