Chemical routes to materials

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Robust fabrication of superhydrophobic and photocatalytic self-cleaning cotton textile based on TiO$_2$ and fluoroalkylsilane

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ABSTRACT

A facile, mild and low-cost approach of the fabrication of self-cleaning cotton textile, which showed excellent superhydrophobic and photocatalytic properties, was proposed. The surface was firstly coated with pure anatase TiO$_2$ through a sol–gel method catalyzed by glacial acetic acid and then modified by (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane (F-17). The hydrophilic cotton textile turned superhydrophobic with a water contact angle of 160.0°. The wettability, surface morphology and chemical composition of pristine and modified textile were investigated, respectively. Meanwhile, the robustness of chemical solutions, laundering treatment and water pressure of the textile were all verified by exposing to different pH solutions, organic solvents, washing and immersing. Importantly, the textile surface showed outstanding self-cleaning performance toward solid pollutant, daily liquids, oil and even organic contaminant, attributing to the synergetic function of superhydrophobicity and photocatalysis of TiO$_2$ nanoparticles. Therefore, the self-cleaning textile is an expected material for daily and industrial applications in diverse conditions, even harsh environment.

Introduction

Self-cleaning surfaces have triggered enormous attention around the globe for the diversity of potential application fields [1, 2]. Currently, there are two mechanisms to create the self-cleaning surfaces:

One is superhydrophobicity and another is photocatalysis [3].

Superhydrophobic surfaces have the compelling competence of repelling water, which requires the WCA > 150° by definition [4, 5]. In this way, the attached stain on surface can be washed away immediately and efficiently by flowing water. Two

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crucial factors of developing the superhydrophobic property are extremely low surface energy and specific surface structures, especially hierarchical textures [6, 7]. Many strategies, including sputter coating [8], plasma treatment [9], chemical vapor deposition [10, 11] and sol–gel route [12, 13], have been adopted. Recently, one of the popular research fields is superhydrophobic textile, demonstrating promising applications in water proofing [14], corrosive resistance [15, 16], flame prevention [17] and self-cleaning [18]. Unfortunately, this type of surfaces would be immediately stained by oil as well as organic contaminants, resulting in the reduction or even loss of superhydrophobicity [19, 20].

Another self-cleaning surface is produced by photocatalytic coating which can chemically degrade organic stain to CO_2 and H_2O under light exposure [21]. Photocatalysis is considered as a clean process, because the degradation process can be accomplished without high temperature, intensive energy and waste residue [22, 23]. TiO_2 has many superiorities compared with other nanoparticles as photocatalysts, such as higher photocatalytic efficiency, chemical stability, availability and competitive cost [24]. The preferable catalytic activity of TiO_2 nanoparticle has been achieved with anatase phase [25]. It is fascinating if a material with both superhydrophobicity and photocatalysis is developed, for it can not only repel water, but also decompose organic stains simultaneously [26]. However, to develop the functional materials with both superhydrophobic and photocatalystic properties is still a challenge for the surface that would either lose its superhydrophobicity under light irradiation or simply show photocatalysis on superhydrophilic surface [27].

The sol–gel method is frequently used to build desired surface roughness [28] and can readily applied on various substrates including steel, wood, sponges, filter paper, glass and fabric, at relatively low or even room temperature [29]. During TiO_2 sols preparation, toxic and corrosive chemicals, including hydrochloric acid and nitric acid, are generally employed as catalysts [30, 31]. These chemicals would cause environmental pollution and destroy the original properties of pristine textile. Moreover, the obtained TiO_2 sols may be a mixture of anatase, rutile and brookite, not pure anatase [32]. Thus, the adoption of milder acid at low temperature is not merely cost-saving, but also favorable for materials

such as cotton that are vulnerable to chemical or thermal condition.

Hitherto, many researchers have diligently devoted to investigate and fabricate self-cleaning surfaces. Afzal et al. [33] prepared a superhydrophobic fabric with TiO_2 and fluorine-free silanes through multi-stepped deposition, showing photocatalytic property in visible light. Huang et al. [34] achieved a robust self-cleaning cotton by hierarchical TiO_2 particles via a hydrothermal reaction and fluoroalkylsilane modification. Deng et al. [35] reported a facile and practical sol–gel method of forming TiO_2–SiO_2 @PDMS multifunctional hybrid films, which gained both superhydrophobicity and photocatalysis. Takashi et al. designed a versatile surface, possessing superhydrophobicity and photocatalytic self-cleaning ability, with polytetrafluoroethylene (PTFE) and TiO_2 as photocatalyst [8]. Nevertheless, it still faces a big challenge for constructing self-cleaning surface exhibiting both superhydrophobic and photocatalytic abilities through a facile and mild process and can be available to large-scale production and application.

In this study, a facile, mild and low-cost sol–gel method to prepare superhydrophobic and photocatalytic textile was proposed. The cotton surface was firstly coated with the anatase TiO_2 sols using glacial acetic acid as catalyst and then modified by (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (F-17), which could render superhydrophobicity due to its low energy hydrophobic groups (–CF_2, –CF_3) [36]. The chemical stability, washing durability and stain resistance of the modified textile were also measured to evaluate the qualification of employing in practical occasions, particularly harsh conditions. This study was also verified its excellent photocatalytic self-cleaning activity by the degradation of colorant oil red.

Experimental

Materials

Titanium tetraisopropoxide (TTIP, 99.9%), anhydrous ethanol (EtOH), N,N-dimethylformamide (DMF), tetrahydrofuran (THF) and acetone (CP) were obtained from Aladdin. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (F-17) was supplied by Jinan LangHua Chemical Co., Ltd. Commercial woven cotton textile (135 × 70 inch^{-1}, 114 g m^{-2})

was purchased from a textile supermarket. The textile was firstly cut into 4 cm × 4 cm pieces and cleaned with anhydrous ethanol and deionized water for three times to remove possible impurities and then thoroughly dried at 80 °C in an oven before experiments. All other chemical reagents were employed as supplied.

Preparation of TiO_2 sols

The method of generating TiO_2 sols was revised moderately from the literature [37]. 2 g TTIP was added dropwise into 50 g deionized water involving 5 g glacial acetic acid with stirring to ensure sufficient reaction, and then, the mixture was kept stirring vigorously at 25 °C for 20 h. The newly prepared TiO_2 solutions had rich precipitation, which turned into transparent sols after reserved without stirring at 25 °C within two weeks.

Fabrication of self-cleaning textiles

The clean cotton textiles were firstly immersed in the as-received TiO_2 sols for 10 min at 25 °C and washed with deionized water for three cycles to remove superfluous TiO_2 sols and then dried at 80 °C for 0.5 h. The modified textile was named as TiO_2@tex. Next, the modified specimens were placed in 1, 2, 4, 6, 8, 10 wt% F-17 methanol solution (20 mL) under ultrasonic processing at 25 °C for 0.5 h. After treatment, the samples were cured at 110 °C for 0.5 h. Subsequently, the coated textiles were rinsed with absolute ethyl alcohol for three times to remove unattached F-17 and dried at 110 °C for 0.5 h. The obtained textiles were designated as TiO_2@tex-F17.

Sample characterization

The crystal phase of TiO_2 was revealed by X-ray diffraction (XRD, Philips X'Pert Pro MPD) with Cu-Kα radiation (0.154 nm), which conducted at 40 kV and 40 mA. The geometric morphologies of textile surfaces were obtained by scanning electron microscopy (SEM, Hitachi S-4800). Element information of surface was determined by an energy-dispersive spectroscopy (EDS, Horiba EX-250) and X-ray photoelectron spectra (XPS) using ESCALAB 250 Xi spectrometer and Al Kα X-ray radiation. The C 1 s peak (284.8 eV) was taken as reference of the binding energy. The water contact angle (WCA) of 4 μL water

droplet was recorded with a contact angle meter (Shanghai Zhong Chen). Each of the WCA data were the average of five values at different positions on every specimen at room temperature and humidity.

Stability evaluation of TiO_2@tex-F17

To study the chemical stability, the TiO_2@tex-F17 was immersed in solutions of different pH values for 48 h. In addition, the chemical stability was further investigated by immersing in EtOH, DMF, deionized water (H_2O), THF and CP under ultrasonic treatment for 2 h (25 °C, 40 Hz). After treatment, the specimens were rinsed with deionized water and dried to test the WCAs. The laundering test was performed using a revised method based on the literature [38]. The TiO_2@tex-F17 was put into a homemade washing device containing water, 0.3 wt% detergent (Blue Moon detergent, obtained from Blue Moon company in China) and several balls with a rotate speed of 350 rpm at 40 °C. Moreover, 15 min was designated as a cycle. The laundered textile was rinsed thoroughly with enough water to remove the absorbed detergent and heated at 80 °C to dry. Then, the WCAs of laundered fabric were measured to investigate the washing durability of the coated textile.

Results and discussion

Preparation of the modified textile

The preparation of the modified textile via a facile and mild sol–gel method is displayed in Fig. 1. TiO_2 sol, which owned numerous of –Ti–OH groups, was firstly acquired by the hydrolysis and condensation reactions of TTIP. During the preparation process, high temperature, toxic and corrosive reagents were deliberately avoided. Thus, this means it could protect the safety of operators, save energy and apply in various materials, especially majority of biomaterials with relative poor thermal resistance.

Generally, TiO_2 owns three crystalline phases, designated as brookite, anatase and rutile [39]. Among these phases, anatase TiO_2 possesses more efficient photocatalytic activity than that of others. The XRD pattern of the acquired TiO_2 was explored and is presented in Fig. 2. The peaks appeared at scattering angles of 25.3°, 37.8°, 48.0° and 54.2°, which corresponded to the (101), (004), (200) and (211)
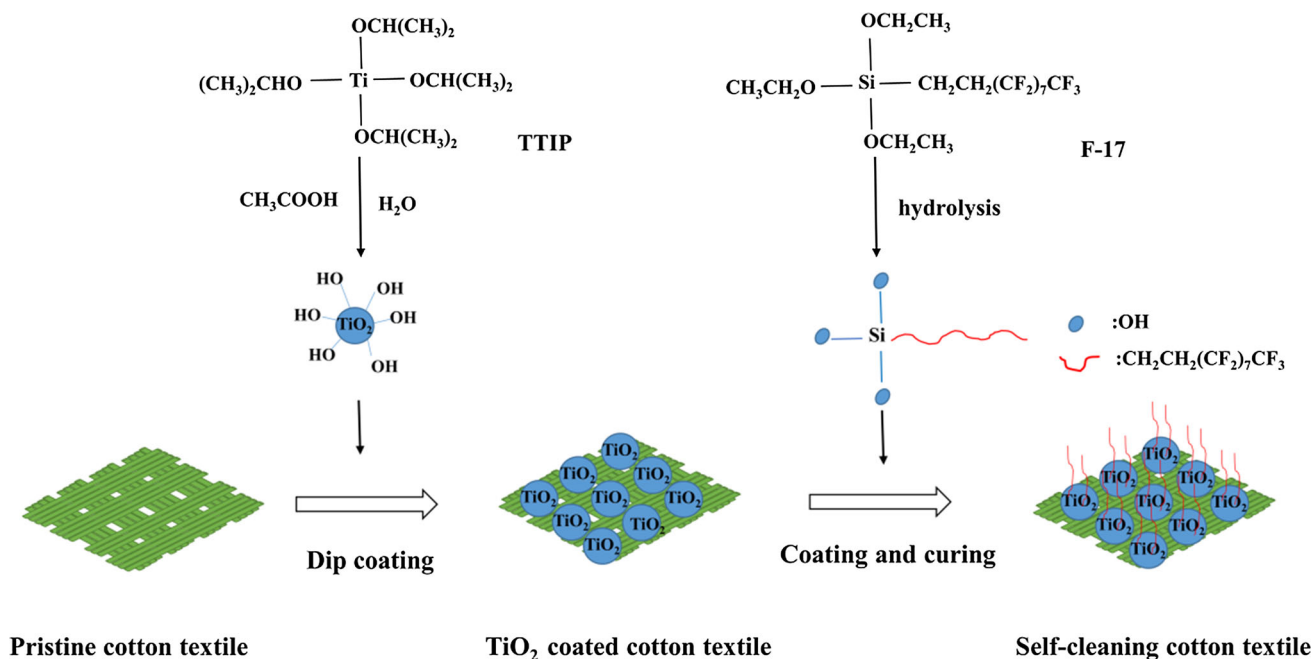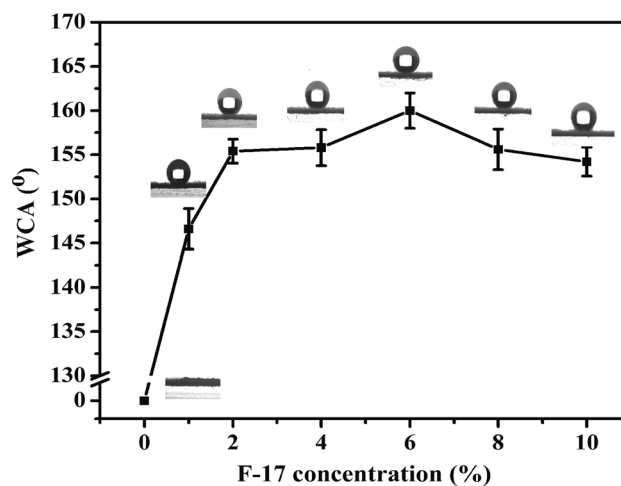
Figure 1 Schematic route of the preparation of modified textile.
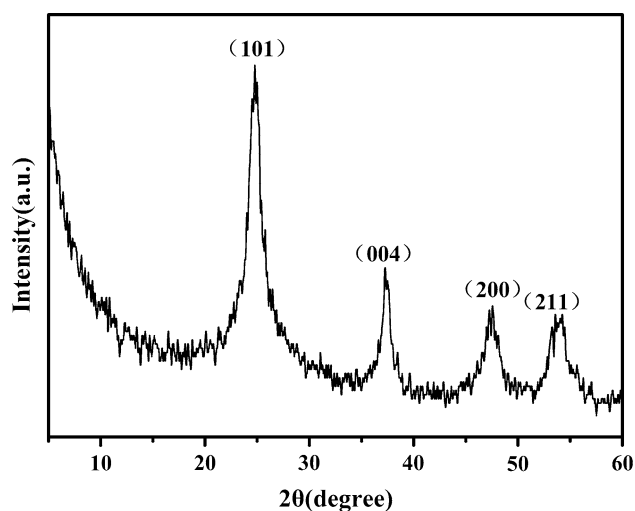
Figure 2 XRD pattern of TiO$_2$.

Figure 3 WCAs of the TiO$_2$@tex-F17 with different concentrations of F-17 solution.

planes featured anatase TiO$_2$ phase, respectively [40]. All diffraction peaks demonstrated the as-received TiO$_2$ nanoparticles were pure anatase phase. Subsequently, the F-17 was coated and cured to endow the TiO$_2$@tex with desirable superhydrophobicity via a facile and mild dip-coating method.

Figure 3 shows the influence of the F-17 concentration on the WCAs of TiO$_2$@tex-F17. The TiO$_2$@tex had a WCA of 0°, exhibiting hydrophilic character caused by the existence of plentiful hydroxyl groups on its surface. With the increase in F-17 concentration

from 1 to 6 wt%, the WCA of TiO$_2$@tex-F17 was enhanced sharply from 146.6° to 160.0° to generate excellent superhydrophobicity. In contrast, the WCA of the pristine textile just modified by F-17 was approximately 120°. However, for TiO$_2$@tex-F17 modified with 10 wt% F-17, in spite of more fluorine content, the WCA was reduced to 154.2°. This result might be caused by partly destruction of the multi-scaled roughness [41]. Taking the WCA and economy into consideration, 6 wt% F-17 solution has been selected and adopted in the following test specimens.

These results verified that the TiO_2 nanoparticles and F-17 were both crucial for superhydrophobicity.

Surface morphology of the modified textile

To investigate the surface morphology of the original cotton, TiO_2@tex and TiO_2@tex-F17, the SEM images of fabric specimens are displayed in Fig. 4. The representative longitudinal fibril surface with natural furrows and veins, which furnished an inherent microscale roughness, could be evidently observed on the pristine fiber (Fig. 4a, b). After being coated by TiO_2 sol, the TiO_2@tex surface exhibited a compact and high-density TiO_2 nanoparticle layer (Fig. 4c–e). In such a case, the roughness of the cotton surface was considerably improved. Figure 4f–h shows SEM images of TiO_2@tex-F17 surface. The constructed surface preserved the original fiber morphology and formed a newly nano-scaled rough structure created by the TiO_2 nanoparticles and F-17, resulting in the appropriate hierarchical roughness for preparing superhydrophobic fabric. Owing to the synergistic effect of the micro-/nano-binary surface and the materials of low surface energy, the TiO_2@tex-F17 exhibited superhydrophobicity with a WCA of 160.0°. The results demonstrated that the TiO_2

nanoparticle and F-17 had been successfully coated on cotton fibers, which was further verified by EDS analysis. EDS mapping images in Fig. 5a–f revealed that TiO_2 and F-17 were not agglomerated, but uniformly distributed on the TiO_2@tex-F17 surface. Only C and O elements were found on the pristine textile (Fig. 5g). However, the F, Si and Ti elements were also detected on TiO_2@tex-F17 surface (Fig. 5h), implying the presence of the TiO_2 nanoparticles and F-17 on cotton fibers.

Chemical composition of TiO_2@tex-F17 surface

The chemical composition changes of cotton specimens before and after treated by TiO_2 nanoparticles and F-17 were further analyzed by XPS. As shown in Fig. 6a, it was obviously observed that pure cotton was composed just by C and O elements. The F, O, Ti, C and Si elements on TiO_2@tex-F17 surface were detected and assigned to five peaks at binding energies of 688.6, 532.8, 291.3, 459.3 and 102.7 eV, respectively [42, 43]. The result was in well accordance with the previous EDS results, which confirmed that TiO_2 nanoparticles and F-17 had been successfully covered on fibers. According to the XPS
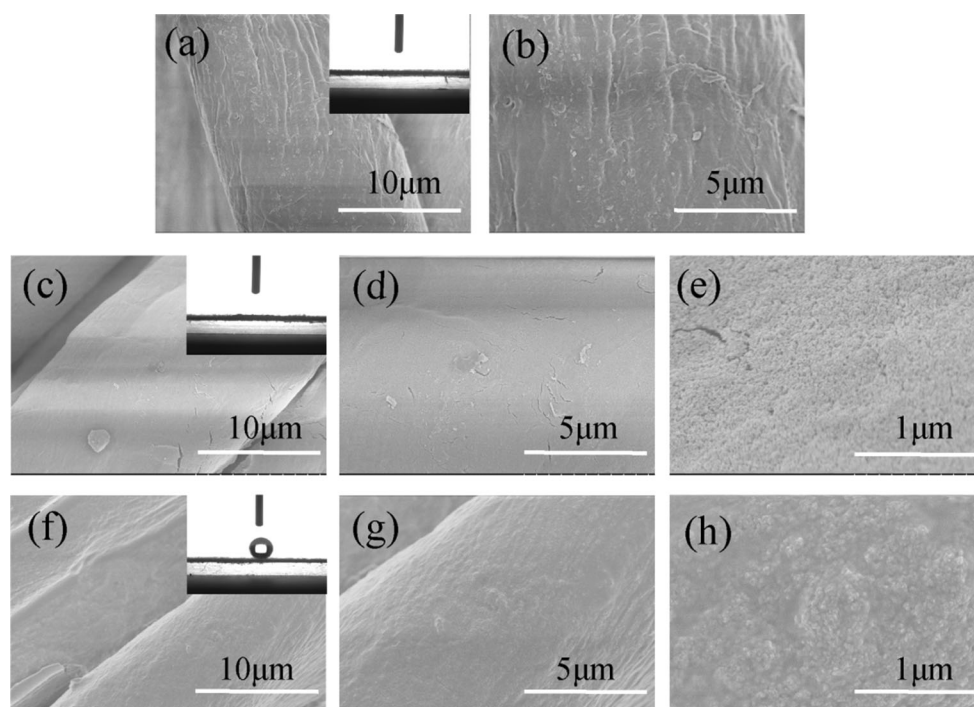
Figure 4 SEM images with different magnifications of **a**, **b** the pristine cotton fabric. **c**–**e** TiO_2@tex. **f**–**h** TiO_2@tex-F17. Inset of **a**, **c** and **f**: photographs of water droplet (4 μL) on the surface of fabrics.

Figure 5 a Low-magnification SEM image of TiO$_2$@tex-F17, **b–f** corresponding elemental mapping. EDS spectrum of the **g** pristine cotton and **h** TiO$_2$@tex-F17.
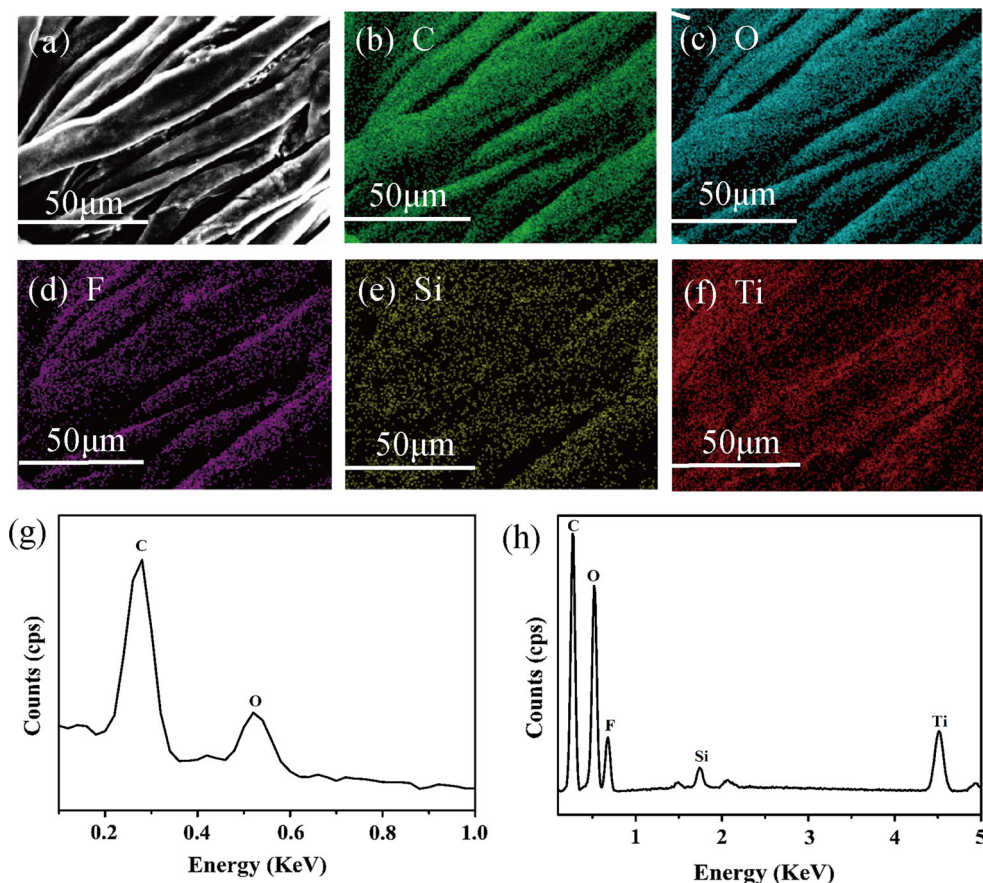
data (Table 1), the atomic ratios of C/O/Ti/F/Si of original cotton and TiO$_2$@tex-F17 were calculated to be 64.31:35.69:0:0:0 and 11.52:7.83:1.72:78.01:0.93:1.47, respectively. The presence of Ti, F and Si of coated textile suggested the successful coating of TiO$_2$ nanoparticles and F-17. Figure 6b shows three peak components curve-fitted by the high-resolution C 1 s peak of pristine textile: C–C (284.7 eV), C–O–H/C–O–C (285.7 eV) and C=O (288.8 eV) [44]. Compared with the pristine textile, the TiO$_2$@tex-F17 displayed two new peaks of C-F$_2$ (291.3 eV) and C-F$_3$ (293.5 eV) (Fig. 6c), indicating the existence of F-17 [45]. The narrow scan of the Ti 2p XPS spectrum is presented in Fig. 6d. Two distinct peaks of Ti 2p were shown at 459.2 and 464.9 eV, which are assigned to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peaks. Moreover, the spin–orbital gap between the two doublets was 5.7 eV, which indicated the normal state of Ti^{4+} [34].

Based on the above results, it could be further verified that the TiO$_2$ nanoparticles and F-17 which provided low surface energy had indeed coated on fibers. Such combination of nano- and microscaled structure and low surface energy material was

favorable to fabricate the superhydrophobic materials, and this was in well accordance with the high WCA of the TiO$_2$@tex-F17.

Durability

Considering the complexity and variety of application situations, the chemical durability of the textile undoubtedly should be tested. Herein, the resistance of TiO$_2$@tex-F17 to solution with different pH values was also investigated. As shown in Fig. 7a, it was obvious that the TiO$_2$@tex-F17 retained superhydrophobicity in different pH values liquids because the WCA was all greater than 150°. The phenomenon may be attributed to the trapped air layer formed on the surface, which could prevent the harm of acid or alkali. This indicated that the TiO$_2$@tex-F17 has excellent stability in both acidic and alkaline conditions.

Besides, the WCAs of the TiO$_2$@tex-F17 decreased slightly after ultrasonication in condition of immersing in a variety of organic solutions, such as DMF, H$_2$O, THF, CP and EtOH (Fig. 7b). This result
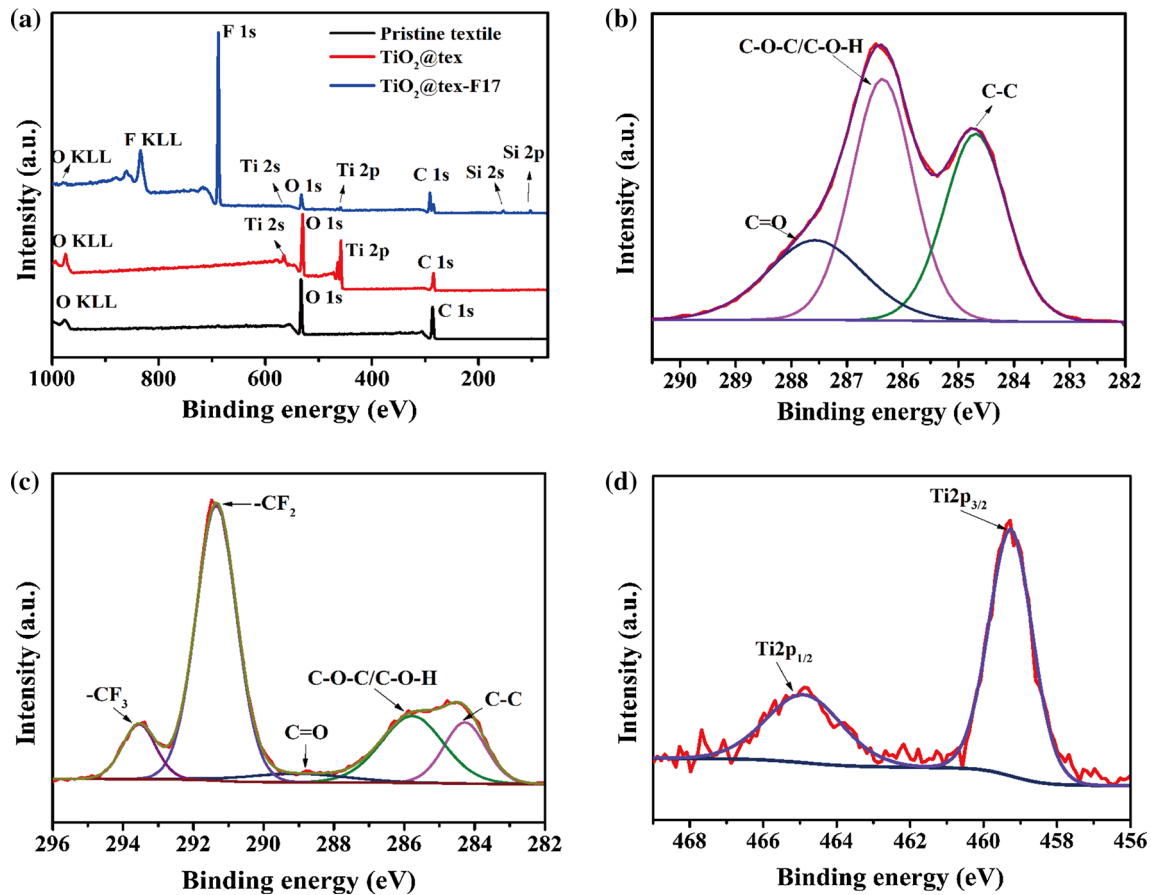
Figure 6 **a** XPS survey spectra of the pristine textile, TiO$_2$@tex and TiO$_2$@tex-F17. **b** C1 s high-resolution spectra of pristine textile and **c**, **d** C1 s, Ti2p high-resolution spectra of TiO$_2$@tex-F17.

Table 1 Chemical composition of textile surface before and after coating

| Sample	Surface concentration (at%)					C/O
	C	O	Ti	F	Si	
Pristine textile	64.31	35.69	–	–	–	1.80
TiO$_2$@tex	12.22	46.83	40.94	–	–	0.26
TiO$_2$@tex-F17	11.52	7.83	1.72	78.01	0.93	1.47

suggested that the TiO$_2$ nanocomposites and F-17 could be covalently bonded to fibers.

As shown in Fig. 7c, the laundering durability of the TiO$_2$@tex-F17 was also evaluated. The laundering test is a comprehensive indicator of the mechanical durability of fabric. After 30 washing cycles, the WCA of TiO$_2$@tex-F17 decreased from 160.0° to 150.1°, which still remained decent hydrophobic performance. The surface element component of TiO$_2$@tex-F17 after various stability tests was measured by XPS (Fig. 7d). The result indicated that no obvious changes occurred on these textile samples after chemical and mechanical treatments. Furthermore, the SEM images showed the compact layer coated on TiO$_2$@tex-F17 was still intact after immersing in acid, alkali solutions and organic solvent (Fig. 7e–g), while the surface appeared slightly damaged after laundering for 30 times (Fig. 7h). In summary, the TiO$_2$@tex-F17 dominates superior resistance against a variety of organic solvents, acid and alkali solutions, as well as washing. The verified desirable durability would undoubtedly expand its application in various fields, even harsh conditions.

Furthermore, to evaluate the performance of bearing a high liquid pressure, TiO$_2$@tex-F17 was forced to immerse into water. A mirror-like surface was apparently visible due to the light reflection of residual air trapped between water and fabrics (Fig. 8b). In contrast, the pristine textile started to absorb water as long as immersed in water due to its
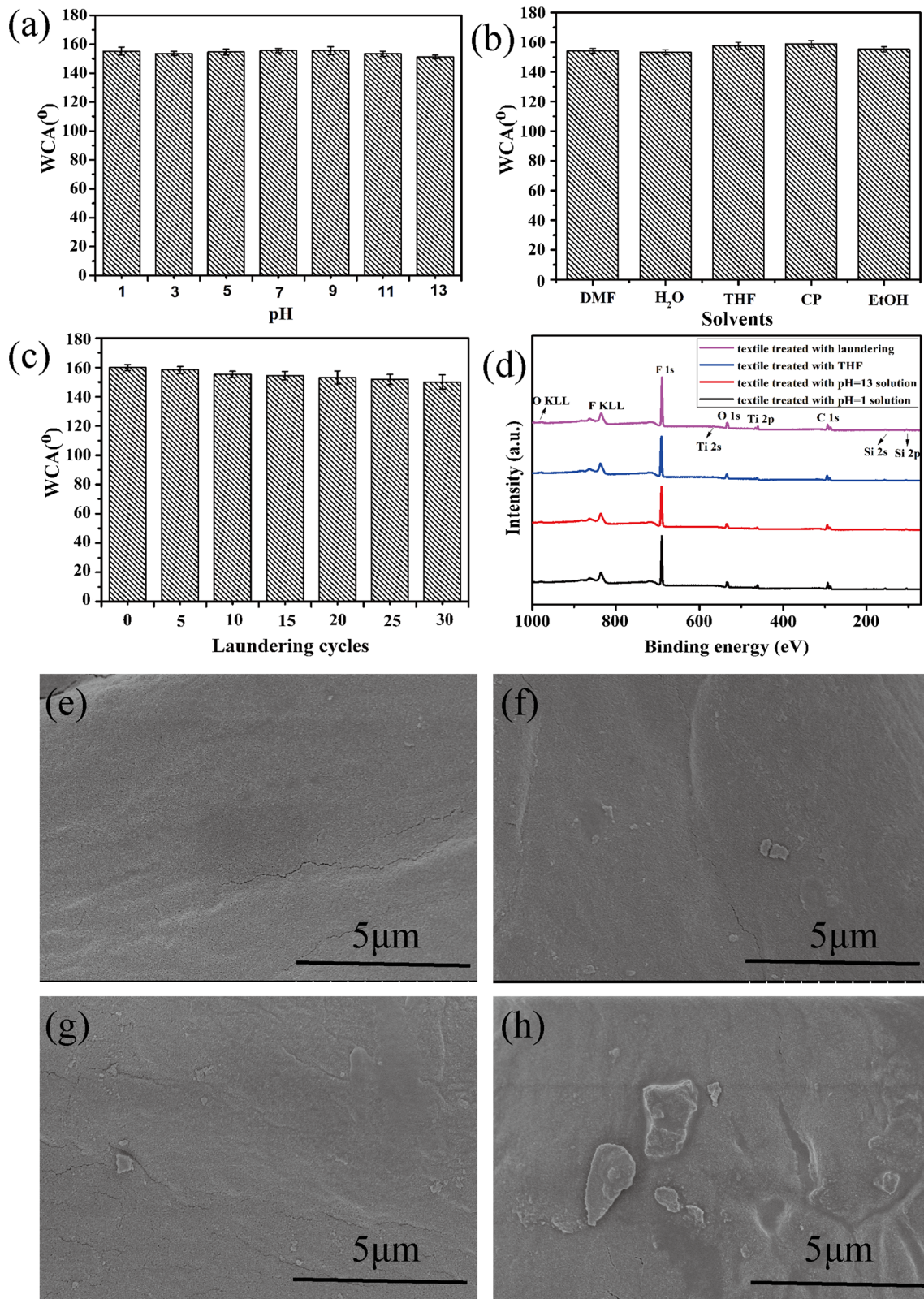
Figure 7 Influence of **a** pH values, **b** different organic solutions and **c** laundering cycles on the WCA of TiO$_2$@tex-F17. **d** XPS and SEM images of TiO$_2$@tex-F17 after treated with **e** pH = 1 solution, **f** pH = 13 solution, **g** THF solvent and **h** laundering (30 cycles).
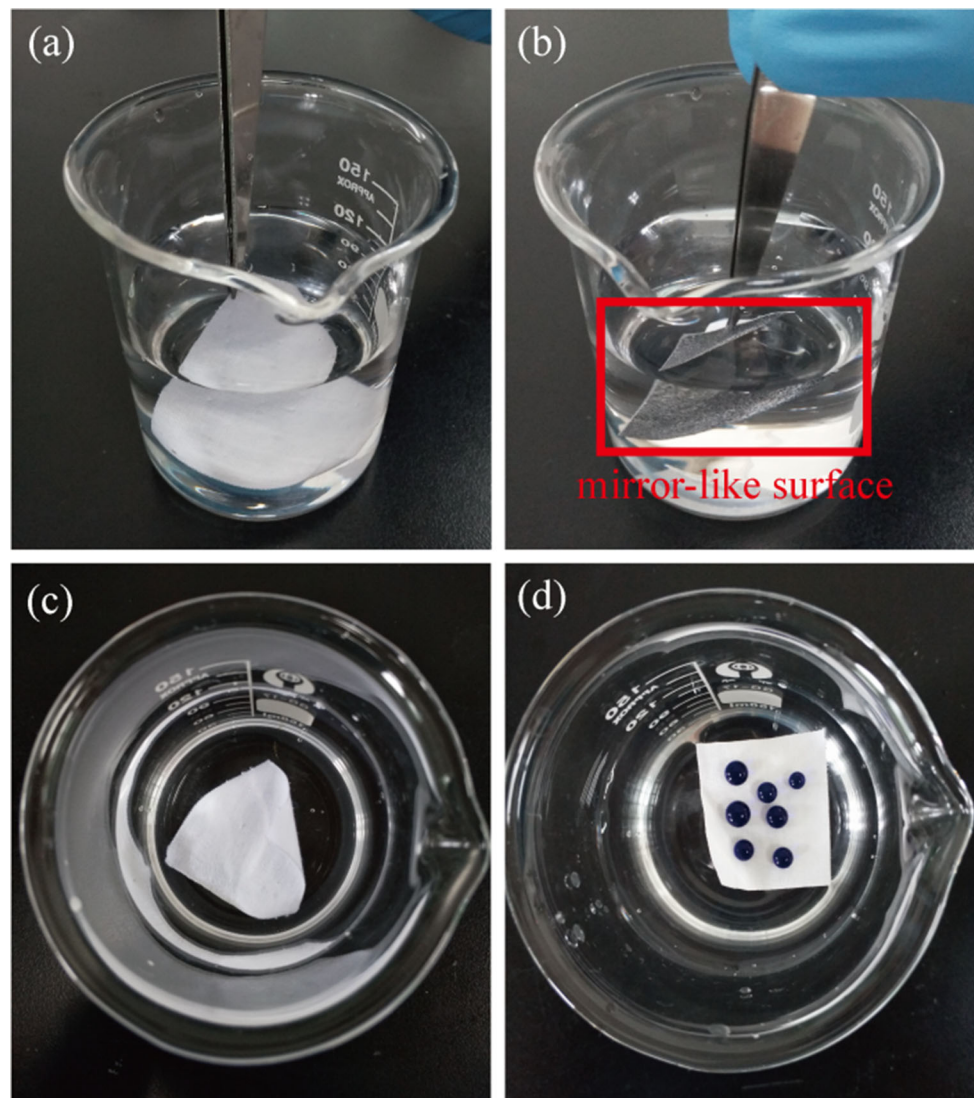
Figure 8 Images of the **a** pristine textile and **b** TiO$_2$@tex-F17 submerged in water. Images of **c** pristine textile in water and **d** TiO$_2$@tex-F17 above water without artificial force.

hydrophilic nature (Fig. 8a) and immediately sunk in the bottom of the beaker without additional force (Fig. 8c). More interestingly, the TiO$_2$@tex-F17 can readily keep floating on water, even though bearing several water droplets on top (Fig. 8d). This indicated that this series of superhydrophobic materials could be employed in shipbuilding industry [46].

Self-cleaning

The superhydrophobic materials with low water adhesion generally possess the capacity of self-cleaning. On account of the unique wettability, water droplets would readily roll off the surface and passingly take away the subsistent contaminants on its surface. The surface should conform with various demands in practical application situations and provide satisfied performance in severe environments. To attest the self-cleaning performance of the TiO$_2$@tex-F17, hydrophilic carbon powder was modeled as pollutant. As shown in Fig. 9, the water droplet hanging on the needle was capable to carry off the carbon powder through touching and moving actions. Meanwhile, the droplet was unable absorbed by surface owing to low adhesive force. Then, the pollutant readily attached on the surface of water droplet, verifying a self-cleaning ability similar to the lotus leaf.
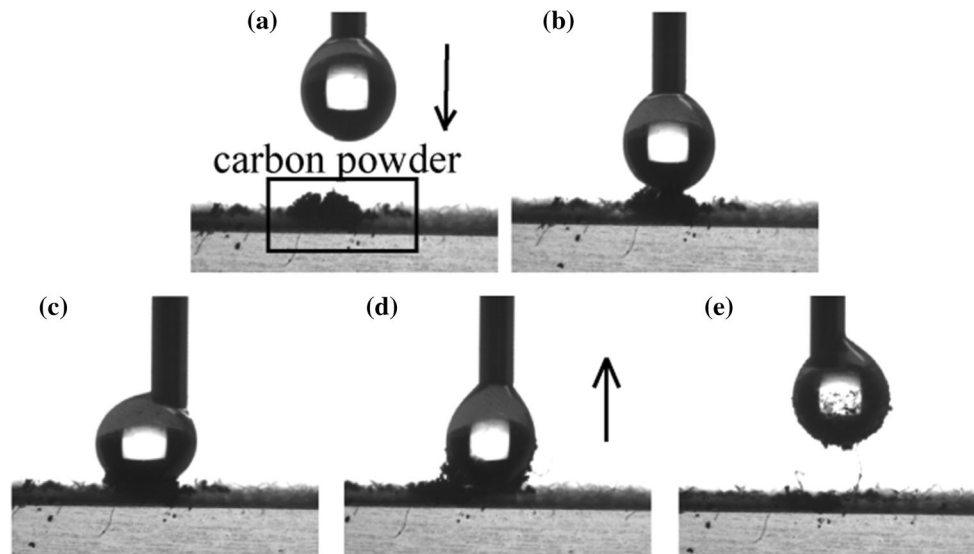
Figure 9 Self-cleaning ability of the TiO$_2$@tex-F17.

Furthermore, a variety of domestic liquid pollutants, including tea, juice, coffee, cola, milk and even soybean oil, were chosen to further evaluate the self-cleaning performance of the TiO$_2$@tex-F17. As shown in Fig. 10, these liquid droplets presented fairly standard spherical shape on the surface of TiO$_2$@tex-F17, demonstrating excellent repellency and anti-fouling property against various daily liquids. It was pleased that these liquids immediately rolled off the coated surface as expected rather than adhere to it, and the surface kept clean as the original textile surface. According to above comprehensive tests, the
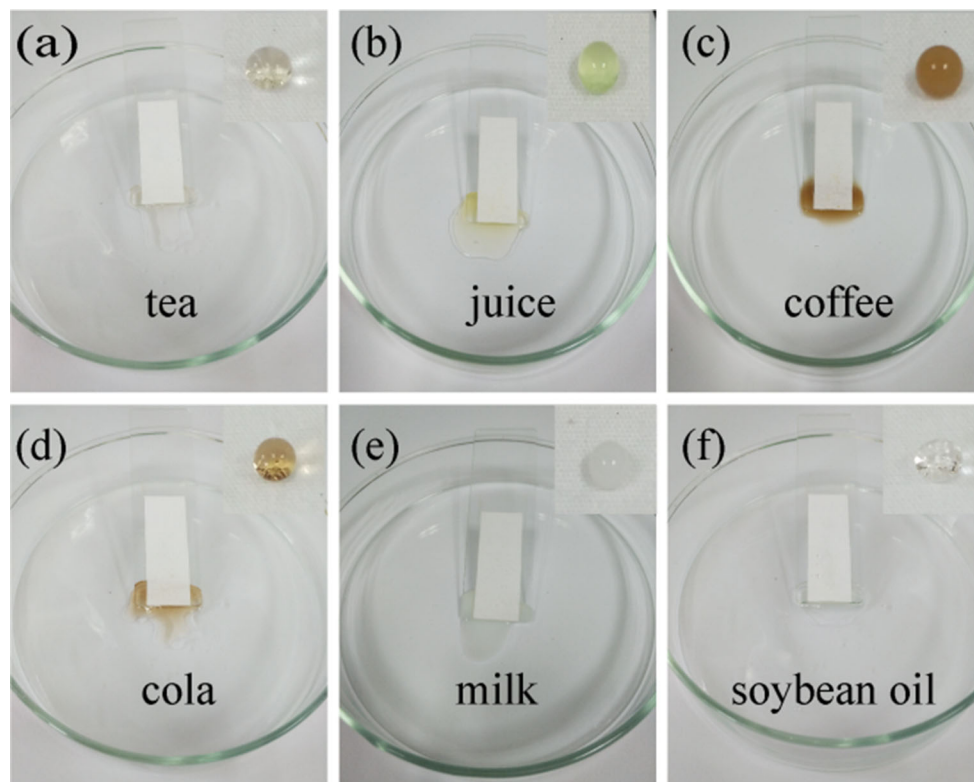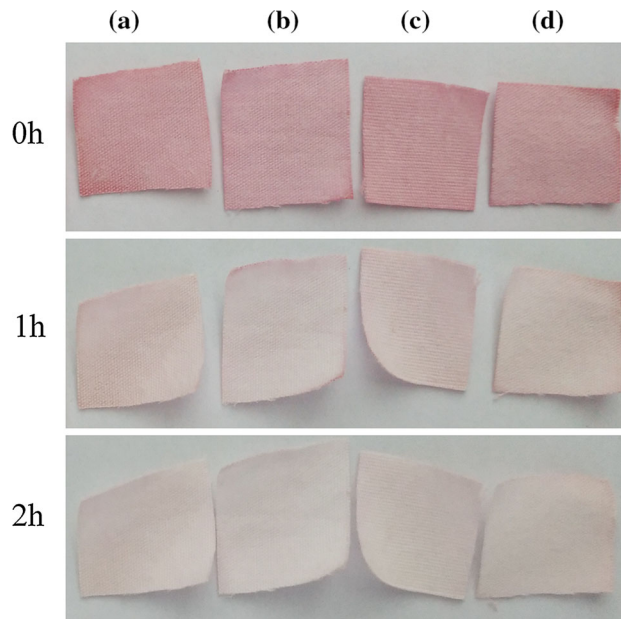

Figure 10 Anti-fouling performance of the TiO$_2$@tex-F17 against liquid pollutants.
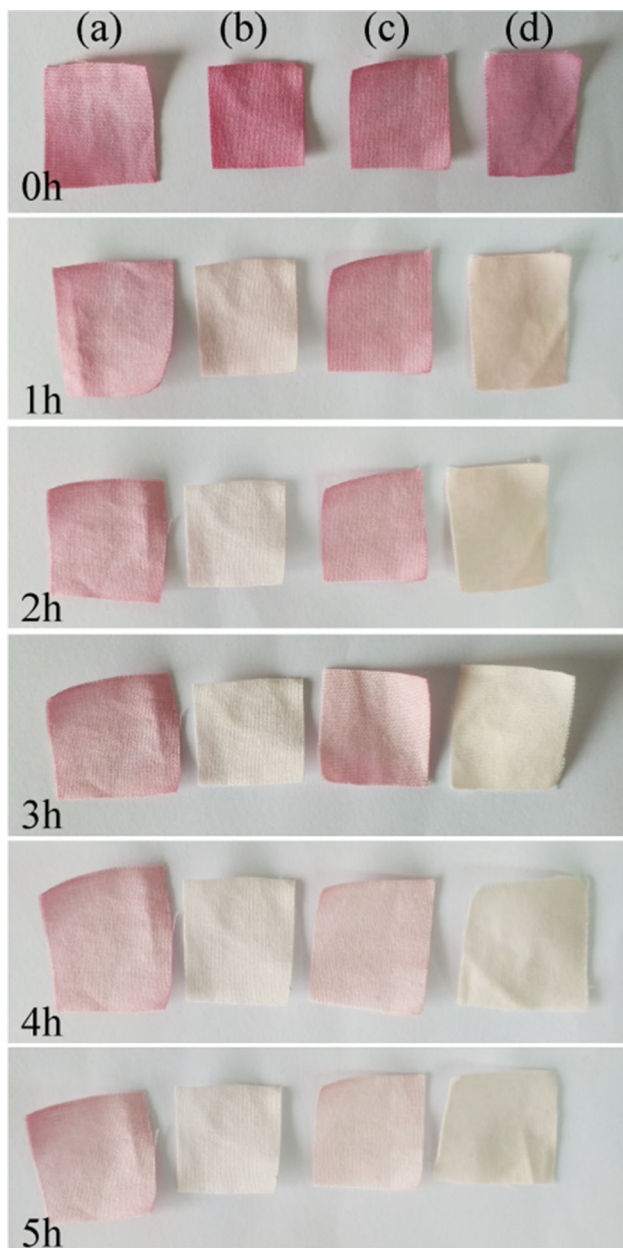
Figure 11 Degradation of white cotton samples stained with oil red on the **a** pristine textile, **b**TiO$_2$@tex, **c** 17F@tex and **d** TiO$_2$@tex-F17 from left to right row successively after 5-h irradiation under UV light.

Figure 12 Degradation of oil red on the TiO$_2$@tex-F17 fabric treated with **a** pH = 1 solution, **b** pH = 13 solution, **c** THF solvent and **d** laundering (30 cycles) from left to right row successively after 2-h irradiation under UV light.

well-pleasing anti-fouling ability of TiO$_2$@tex-F17 was definitely confirmed. Therefore, the coating can be extensively applied in other daily application fields, such as household products and wall decoration, which expected anti-fouling ability.

The photocatalytic performance of the TiO$_2$@tex-F17 under UV irradiation (20 mW cm^{-2}) was also investigated. The photo-induced degradation of the

oil red on cotton under UV irradiation is shown in Fig. 11, which displays the efficient photocatalytic activity of both TiO$_2$@tex and TiO$_2$@tex-F17. The stain of oil red on the TiO$_2$@tex-F17 almost disappeared after UV irradiation for merely 1 h, as quickly as TiO$_2$@tex. However, the red stain of oil red on pristine cotton and 17F@tex was still clearly visible even exposed to UV light for 5 h. Importantly, the TiO$_2$@tex-F17 still maintained excellent photocatalytic performance even after treated with acid and basic solution, organic solvent and laundering test. As shown in Fig. 12, the stained red color in these treated samples nearly disappeared after 2 h UV irradiation, which was in accordance with the original TiO$_2$@tex-F17 sample (Fig. 11b). Therefore, the self-cleaning performance for stain removal is comparably desirable.

All in all, the coated textile was prepared via a facile and low-cost procedure, which is comparable and even superior in superhydrophobicity, stability and self-cleaning property than previous reported research [33–35]. And the superhydrophobic coating has great potential in application of other substrates to fabricate novel multi-functional materials.

Conclusions

In this study, we proposed a facile, mild and low-cost sol–gel method for the preparation of superhydrophobic and photocatalytic self-cleaning cotton fabric. The surface was firstly coated by the TiO_2 sols using acetic acid as catalyst and then hydrophobilized by F-17. The WCA of the coated fabric could reach as high as 160°. Furthermore, due to the excellent durability and stain resistance of TiO_2@tex-F17, the resultant fabric could be employed in practical occasions, particularly harsh conditions. The as-received textile has attracting self-cleaning for superhydrophobicity and photocatalysis, which endowed the material potential application in broad filed.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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