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ORIGINAL RESEARCH

Fabrication of UV-resistant and superhydrophobic surface on cotton fabric by functionalized polyethyleneimine/SiO_2 via layer-by-layer assembly and dip-coating

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Abstract In this research, a water-soluble ultraviolet (UV) absorber (PEI-H) was synthesized by grafting polyethyleneimine (PEI) with 2,4-dihydroxybenzophenone (UV-0). UV-resistant and superhydrophobic coating was fabricated upon cotton fabric by sequentially depositing PEI-H, silica sol (SiO_2) and hexadecyltrimethoxysilane via layer-by-layer assembly and dip-coating. The surface morphology, chemical composition, water-repellence, UV resistance property, durability against washing and abrasion test, air permeability as well as safety of the obtained fabric were investigated. It found that the obtained cotton fabric exhibited superior UV-resistant property with UPF value more than 800 which was attributed to the synergistic effect between organic UV absorber (UV-0) and inorganic UV shielding agent (SiO_2). Meanwhile, it also possessed superhydrophobicity, self-cleaning and anti-fouling properties with water contact angle of 154°. In addition, the multifunctional fabric after 20 washing times or 300 abrasion times remained excellent hydrophobicity and the corresponding UPF values were still 400+, showing an outstanding durability. Importantly, the obtained fabric was absolutely safe for human body.

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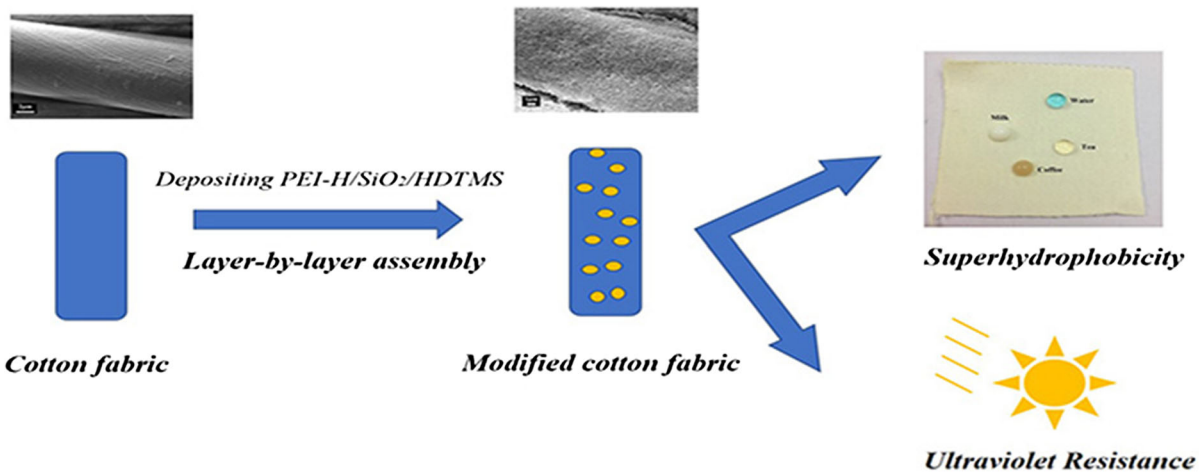
Graphic abstract



Keywords Polyethyleneimine · UV absorber · Silica · Superhydrophobic · UV-resistant · Cotton fabric

Introduction

The ultraviolet rays on the Earth become much stronger than before due to the emergence of the ozone hole. Among the textile fibers, the UV resistance property of cotton fabrics is relatively poor. Especially for those thin and light-colored garments used in summer, the UV resistance of fabric is too weak to protect human skin from UV damage (Davis et al. 1997). Recently, research on multifunctional fabrics has emerged in an endless stream (Lu et al. 2019; Li et al. 2019; Zhao et al. 2019). Fabrics which possess both UV-resistant and superhydrophobic properties are needed in the outdoor field.

So far, those semiconductor oxides such as ZnO (Ren et al. 2018; Chen et al. 2018) and TiO_2 (Huang et al. 2015; Mai et al. 2018) nanoparticles have been widely used in the preparation of superhydrophobic and UV-resistant fabrics owing to their outstanding UV resistance property. However, time-consuming and complex treatments must be employed to suppress their photocatalytic activity since it may cause damage to the substrate and coating after long-term use (Xue et al. 2011; Wang et al. 2011). In addition to these inorganic nanoparticles, organic UV absorbers such as benzophenones, benzotriazoles and substituted triazine derivatives are also able to impart excellent UV-resistant property to cotton fabric (Wang and Hauser 2010; Shen et al. 2014), but they cannot construct the micro- and nano structure which is necessary for superhydrophobic surfaces.

Nano-silica has been widely utilized in the studies about superhydrophobic fabrics due to its advantages of being non-toxic, harmless and inexpensive (Wang and Guo 2019). Besides, nano-silica is one of the inorganic UV shielding agents without photocatalytic activity yet has been rarely applied in the UV protection finishing of fabrics as a result of the relatively weak UV resistance property. Hence, the simultaneous introduction of nano-silica and organic UV absorbers onto the surface of the fabric can create conditions for the fabric to achieve both superhydrophobic and UV-resistant properties.

Layer-by-layer (LbL) assembly is a versatile and simple technique to fabricate multilayer coatings on fabrics (Zhang et al. 2018; Apaydin et al. 2015). Polyethyleneimine (PEI) is a common cationic polyelectrolyte in electrostatic self-assembly (ESA) with strong reactivity because of abundant amino groups ($-NH_2$). Grafting the organic UV absorber onto polyethyleneimine will not only improve the thermal stability of UV absorber but also impart UV-resistant property to PEI.

Herein, a water-soluble UV absorber (PEI-H) was synthesized. The superhydrophobic and UV-resistant cotton fabric was obtained by dipping in positively

charged PEI-H aqueous solution and negatively charged silica sol followed by dipping in hexadecyltrimethoxysilane (HDTMS) solution. PEI-H acted not only as a cationic polyelectrolyte in LBL but also as an organic UV absorber. Simultaneously, SiO_2 worked as inorganic UV shielding agent in addition to forming rough structure on the surface of cotton fabrics. The UV resistance performance of fabrics was significantly enhanced due to the synergistic effect between PEI-H and SiO_2. After further modification with HDTMS, superhydrophobic property was also obtained.

Experimental

Material

Polyethyleneimine (PEI, Mw = 600), hexadecyltrimethoxysilane (HDTMS) and tetraethyl orthosilicate (TEOS) were purchased from McLean Reagent Co., Ltd (Shanghai, China). 2,4-Dihydroxybenzophenone (UV-0) was obtained from Mylar Chemical Technology Co., Ltd (Shanghai, China). Epichlorohydrin was obtained from Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Cotton fabric was supplied by Jinfang Group Co., Ltd (Guangdong, China). Cotton fabrics were ultrasonically washed three times with ethanol and kept dry in air.

Synthesis of PEI-H

2-Hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) was synthesized according to a previous literature (Manasek et al. 1976). Polyethyleneimine (1 g, 10 ml H_2O) and HEPBP (0.5 g, 10 ml THF) reacted at 40 °C for 12 h. The obtained mixture was adjusted to pH 3–4 with hydrochloric acid and then precipitated three times with 300 ml ethanol. The product was kept in a vacuum oven at 50 °C for 3 h after centrifugation. Finally, the yellow viscous liquid (PEI-H) was obtained (Fig. 1a). FTIR (KBr) (cm^{-1}): 3300 (νN–H), 1623 (νC=O), 1268 (νC–O), 776,697 (νAr–H). ^{1}H NMR (600 MHz, D_2O) δ 7.50 (dd, J = 59.8, 52.4 Hz, 6H), 6.55 (s, 2H), 4.15 (dd, J = 100.3, 72.4 Hz, 2H), 3.63–2.46 (m, 159H) (Figs. S1 and S2).

Synthesis of SiO_2 sol

The SiO_2 sol was prepared according to Stober method (Li et al. 2016). Concisely, 250 ml ethanol, 15 ml ammonium hydroxide and 5 ml deionized water were poured into three-necked flask. After stirring at 50 °C for 30 min, 14 ml tetraethylorthosilicate (TEOS) was added and the mixture kept stirring overnight.

The preparation of modified cotton fabrics

The cotton fabric was firstly immersed into PEI-H aqueous solution (0.2 g, 20 ml H_2O) for 3 min, then rinsed with water and dried at 80 °C. Secondly, the fabric with positive charges was immersed in SiO_2 sol (20 ml) for 5 min. After being rinsed with water and dried at 80 °C, the fabric with one layer of (PEI-H/SiO_2) was obtained. Repeat the above operations for n times and $(PEI\text{-}H/SiO_2)_n$ fabric was obtained.

The $(PEI\text{-}H/SiO_2)_n$ fabric was subsequently dipped in HDTMS ethanol solution(1 g, 30 ml) for 1 min and dried at 80 °C. After being cured at 130 °C for 5 min, a superhydrophobic and UV-resistant coating was fabricated on cotton fabric (Fig. 1b).

Characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out on American FTS-3000 infrared spectrometer in the optical range 400–4000 cm^{-1}. ^{1}H NMR spectra was recorded by Varian Mercury Vx-600 spectrometer at 600 MHz. The surface morphology and chemical composition of the fabric were examined by a LEO1530VP (provided by Zeiss in Germany) and X-ray photoelectron spectroscopy (Kratos Axis Ulra DLD, UK) with Mg Kα monochromatic X-ray source, respectively. The measurement of water contact angle (WCA) was carried out by a contact angle meter (JC2000D1) using 5 μl water droplet. A According to AS/NZS 4399:1996, T(UVA), T(UVB) and UPF of fabrics were measured by Cary 5000 UV–Vis Spectrophotometer (Agilent, America) equipped with an integrating sphere. Air permeability, thickness and bending rigidity of cotton fabric were obtained by using FX-3300 air permeability testing instrument (TEXTEST, Switzerland), YG 141 fabric thickness instrument (Shuanggu, China) and YG (B) 022 automatic fabric stiffness instrument (Jigao, China),

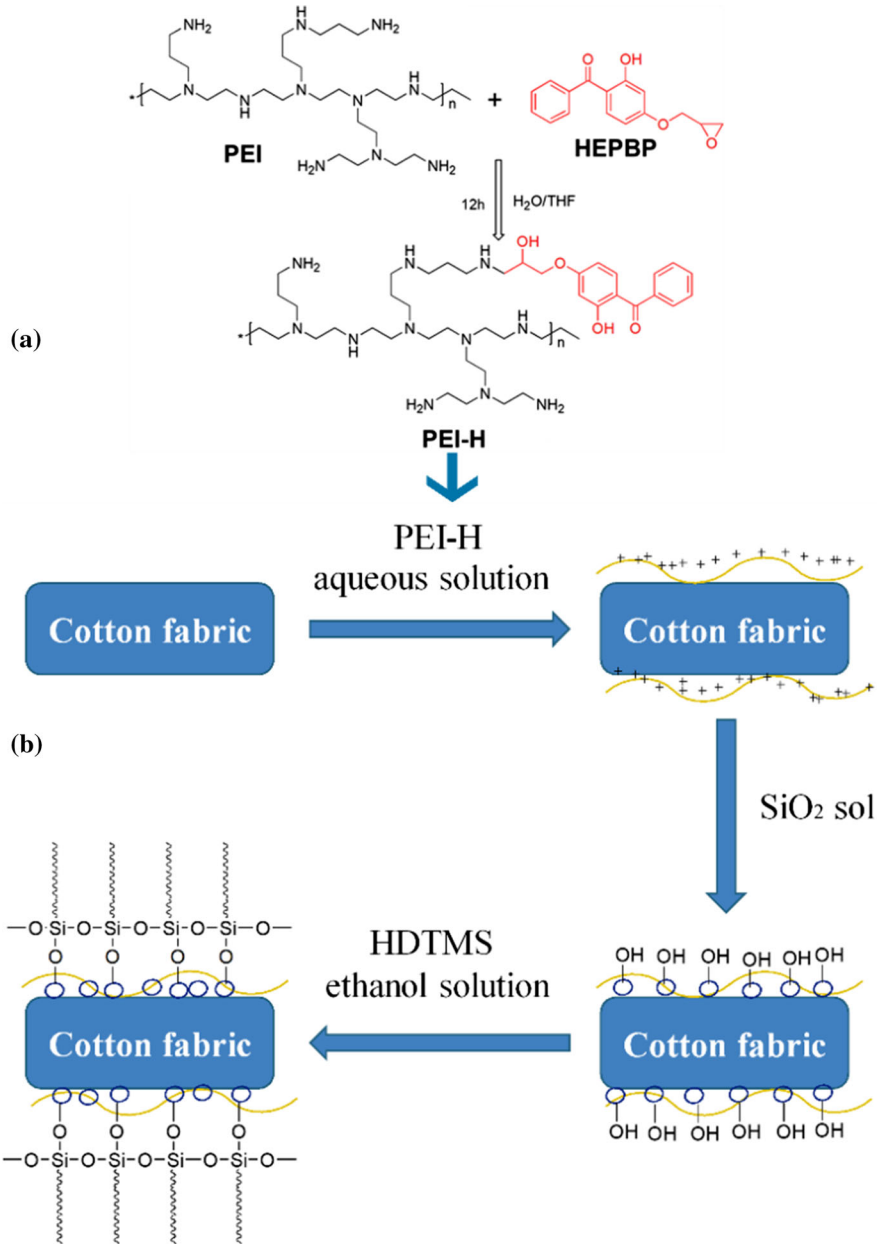


Fig. 1 The synthesis step of PEI-H (**a**). Schematic representation of the preparation process of multifunctional cotton fabric (**b**)

respectively. Safety of cotton fabric were tested based on Standard 100 by OEKO-TEX" (2018).

Washing test was carried out according to AATCC Test Method 61-2006 (No 2A). Fabrics were washed using a SHA-B laundering machine (Wuhan, China) at 49 °C together with 50 stainless steel balls and detergent.

Abrasion test was conducted by using a 1000 mesh sandpaper with load pressure at 100 g. The fabric was kept in direct contact with sandpaper and moved for 20 cm at the speed of 4 cm/s.

Results and discussion

Surface morphology and chemical composition

As shown in Fig. 2, SiO_2 sol was negative with a zeta potential of − 45.2 mv and the average size of SiO_2

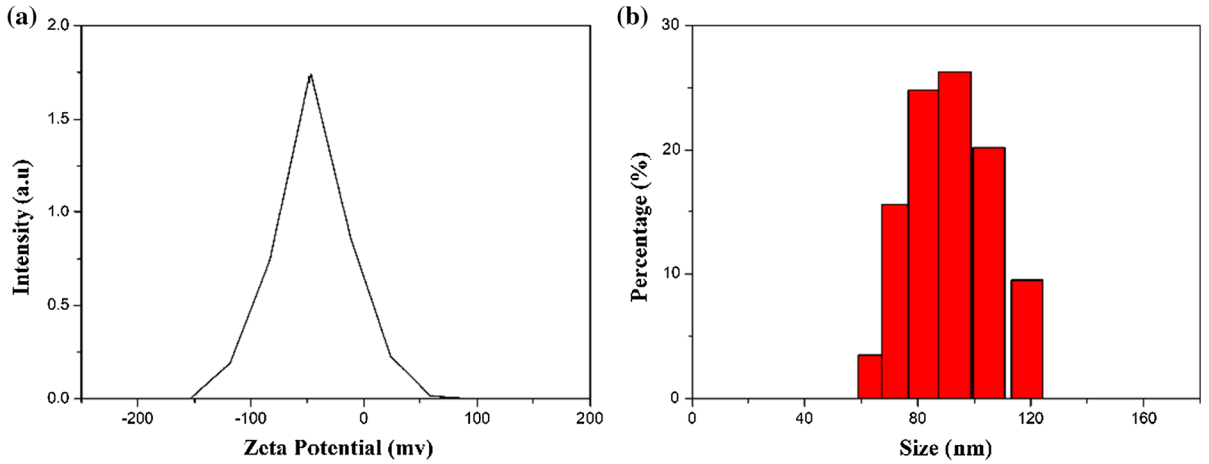


Fig. 2 Zeta potential (**a**) and size (**b**) of SiO_2 nanoparticles

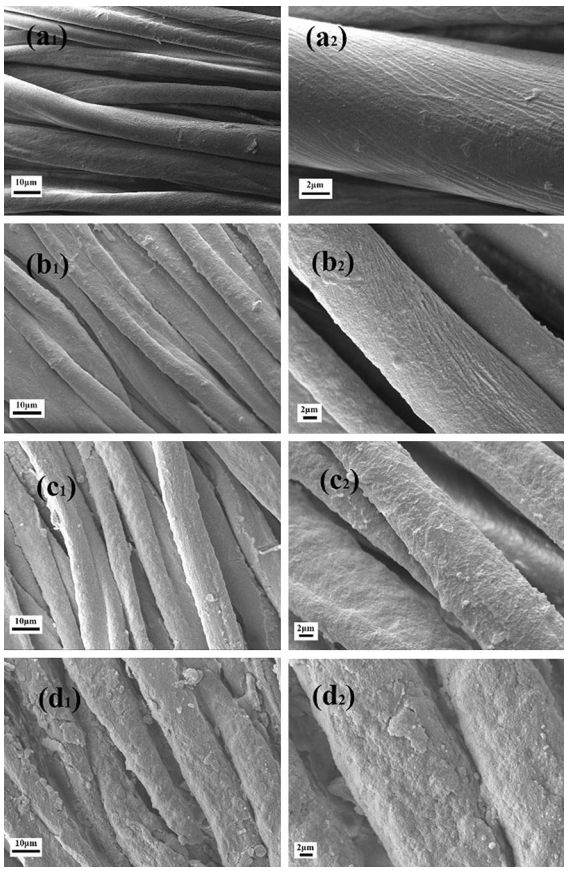


Fig. 3 SEM images of pristine fabric ($\mathbf{a_1}$, $\mathbf{a_2}$), $(PEI\text{-}H/SiO_2)_1$@HDTMS fabric ($\mathbf{b_1}$, $\mathbf{b_2}$), $(PEI\text{-}H/SiO_2)_3$@HDTMS fabric ($\mathbf{c_1}$, $\mathbf{c_2}$) and $(PEI\text{-}H/SiO_2)_5$@HDTMS fabric ($\mathbf{d_1}$, $\mathbf{d_2}$)

nanoparticles was 86 nm. Figure 3 depicts the surface morphologies of pristine and modified cotton fabrics. The pristine fabric exhibited a smooth surface with natural texture. Nano-silica formed a micro- and nano-scale structure on the surface of modified fibers. In addition, the amount of SiO_2 nanoparticles attached on fibers increased with the assembling layers. After being assembled with 5 layers, a large amount of silica particles also appeared in the gaps between fibers. However, due to the excessive number of particles on the surface of the fiber, the outermost layer of silica particles adhered loosely to the fiber, resulting in low adhesion of the coating. Therefore, the number of assembling layers should be less than 5.

XPS measurement was used to further investigate the surface chemical composition of cotton fabrics (Fig. 4). Compared to the pristine fabric, new peaks at 153 eV (Si 2s),101 eV (Si 2p) and 399 eV (N 1s) appeared in the spectrum of $(PEI\text{-}H/SiO_2)_3$ fabric, with atomic percentage of 12.41% and 1.57%. Furthermore, the N 1s spectrum can be resolved into three components at peaks at 398.3, 399.4 and 400.6 eV, which were assigned to the C–N–C, $N\text{–}(C)_3$ and N–H groups, respectively (Jin et al. 2015; Liu et al. 2015; Zhong et al. 2018). The results indicated the successful introduction of PEI-H and SiO_2 on the surface of cotton fabric.

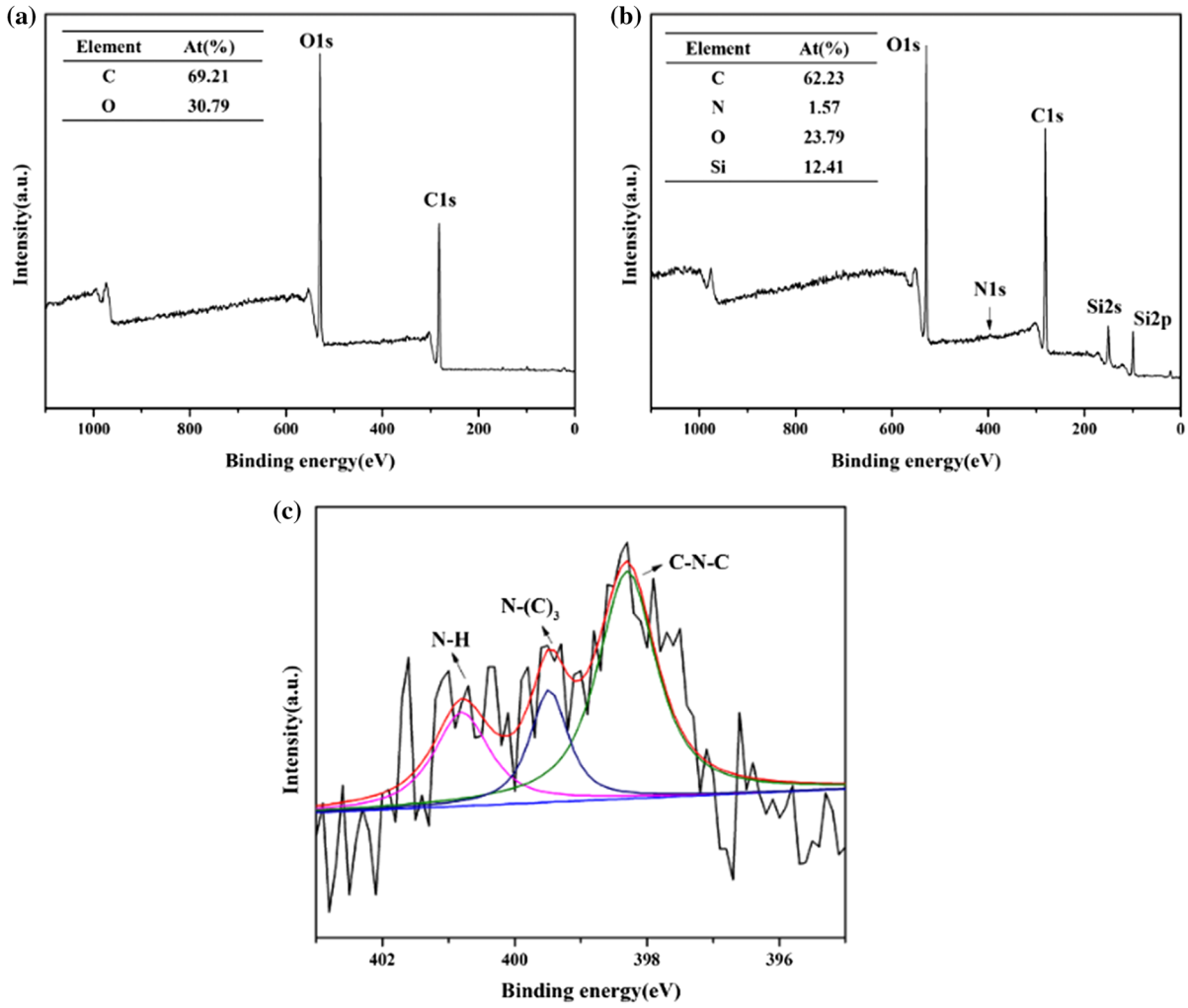


Fig. 4 XPS spectra of pristine fabric (**a**), $(PEI\text{-}H/SiO_2)_3$ fabric (**b**) and N1s high resolution spectrum (**c**)

Surface wetting property

The surface wetting behavior of the modified fabrics were examined by water contact angle and sliding angle. As shown in Fig. 5a, the cotton fabric only treated with HDTMS had a WCA of 136°. After introducing nano-silica, cotton fabrics achieved superhydrophobicty with a maximum WCA of 154° and SA of 6°. According to Wenzel and Cassie-Boxer theories, the hydrophobicity can be enhanced by increasing the roughness of a hydrophobic surface (Cassie and Baxter 1944). The treatment of HDTMS allowed the fabric to undergo a hydrophilic to hydrophobic transition. After the assembly process, the micro-agglomerated nano-silica could form micro- and nano-structure on the surface of the fabric which further improved the hydrophobic properties of cotton fabric and then cotton fabric became superhydrophobic.

In addition, images of other liquid droplets including tea, coffee and milk on the modified cotton fabric were also displayed in Fig. 6b. All these droplets on superhydrophobic fabric presented a sphere shape, attributing to the good liquid repellence of the obtained fabric. Self-cleaning and anti-fouling abilities are also important in practical situation. To demonstrate the self-cleaning property, pristine and modified fabrics were both covered with blue dye, as presented in Fig. 6c. In contrast to the pristine fabric, the blue dye could roll off the surface of the modified fabric with the flow of water without staining the

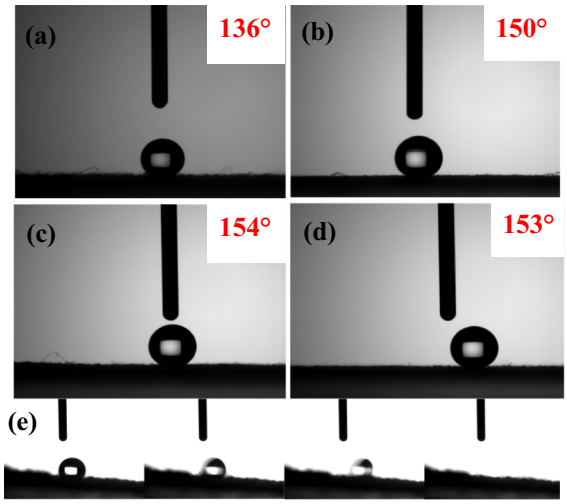


Fig. 5 WCA images: **a** fabric treated with HDTMS; **b** (PEI-H/SiO_2)$_1$@HDTMS; **c** (PEI-H/SiO_2)$_3$@HDTMS; **d** (PEI-H/SiO_2)$_5$@HDTMS. **e** SA images of (PEI-H/SiO_2)$_3$@HDTMS

surface, and the fabric exhibited good self-cleaning property. The anti-fouling property of cotton fabric was illustrated in Fig. 6d. Pristine and the modified fabrics were immersed in liquids including milk, tea and coffee for 1 min. While pristine fabrics were completely wetted and stained, none of these three liquids could wet the surface of the modified fabric and therefore had no significant effect on the fabric surface. The results demonstrated the outstanding self-cleaning and anti-fouling properties of the modified fabric.

UV-resistant property

T(UVA), T(UVB) were measured and UPF value was calculated to evaluate the UV resistance property of cotton fabrics. Figure 7 showed the UV transmittance of the pristine and modified fabrics within wavelengths ranging from 290 nm to 400 nm and corresponding T(UVA), T(UVB) and UPF values were listed in Table 1. The UPF value of pristine cotton fabric was only 9.80, displaying a poor UV resistance property. After being assembled with 5 layers, the UPF value of cotton fabric drastically rose from 9.80 to 876.13, exhibiting superior UV-resistant property.

In addition, (PEI/SiO_2)$_1$@HDTMS fabric was obtained by depositing cotton fabric in PEI solution and silica sol followed by dipping in HDTMS solution. According to Table 1, there was a big difference between the UPF values of (PEI/SiO_2)$_1$@HDTMS and (PEI-H/SiO_2)$_1$@HDTMS fabrics, the latter (390.67) was about 20 times of the former (20.95). The results showed that the silica nanoparticles could shield a small part of the UV rays, and the UV absorber (UV-0) could absorb a larger part of the UV rays. It was the combination of the two effects that improved the UV protection performance of the fabric significantly.

Table 2 showed the UPF values of our as-prepared and other reported UV-resistant cotton fabrics. As far as I know, the UV protectants used in previous studies are either organic UV absorbers (Nos. 9–12) or inorganic UV shielding agents (Nos. 1–8). Obviously, our as-prepared fabric possesses the highest UPF value as a result of the synergistic effect of nano-silica and UV-0. As Table 2 shows, some of those fabrics also have excellent UV resistance property, such as No. 1 fabric, but graphene is relatively expensive. Moreover, our as-prepared cotton fabrics obtain both UV-resistant and superhydrophobic properties by using cheap and safe materials. Hence, this study provides a new idea for the preparation of multifunctional fabrics.

Washing resistance

The durability of the (PEI-H/SiO_2)$_3$@HDTMS fabric was measured by the washing test. One washing cycle continued for 45 min and was approximate to 5 commercial washing cycles. As shown in Fig. 8, although the WCAs of modified fabrics declined from 154° to 147° after 20 washing times, it still was well beyond 140°, manifesting a high hydrophobicity. According to the SEM image of cotton fabric after 20 washing times, the decrease of WCAs was due to the removal of micro- and nano- structure formed by PEI-H/SiO_2.

Figure 9 and Table 3 showed the UV resistance property of modified fabrics after washing test. After 20 washing times, the UPF value of (PEI-H/SiO_2)$_3$@-HDTMS fabric decreased from 686.63 to 427.67, still beyond 400. Since even if part of the nano-silica peeled off, there was still a considerable amount of nano-silica adhering to the fiber. Besides, the PEI-H coated on the surface of the fabric was still sticking to the fiber, which played an important role in the UV protection of the fabric. The results proved that the (PEI-H/SiO_2)$_3$@HDTMS fabric could withstand at least 20 washing times.

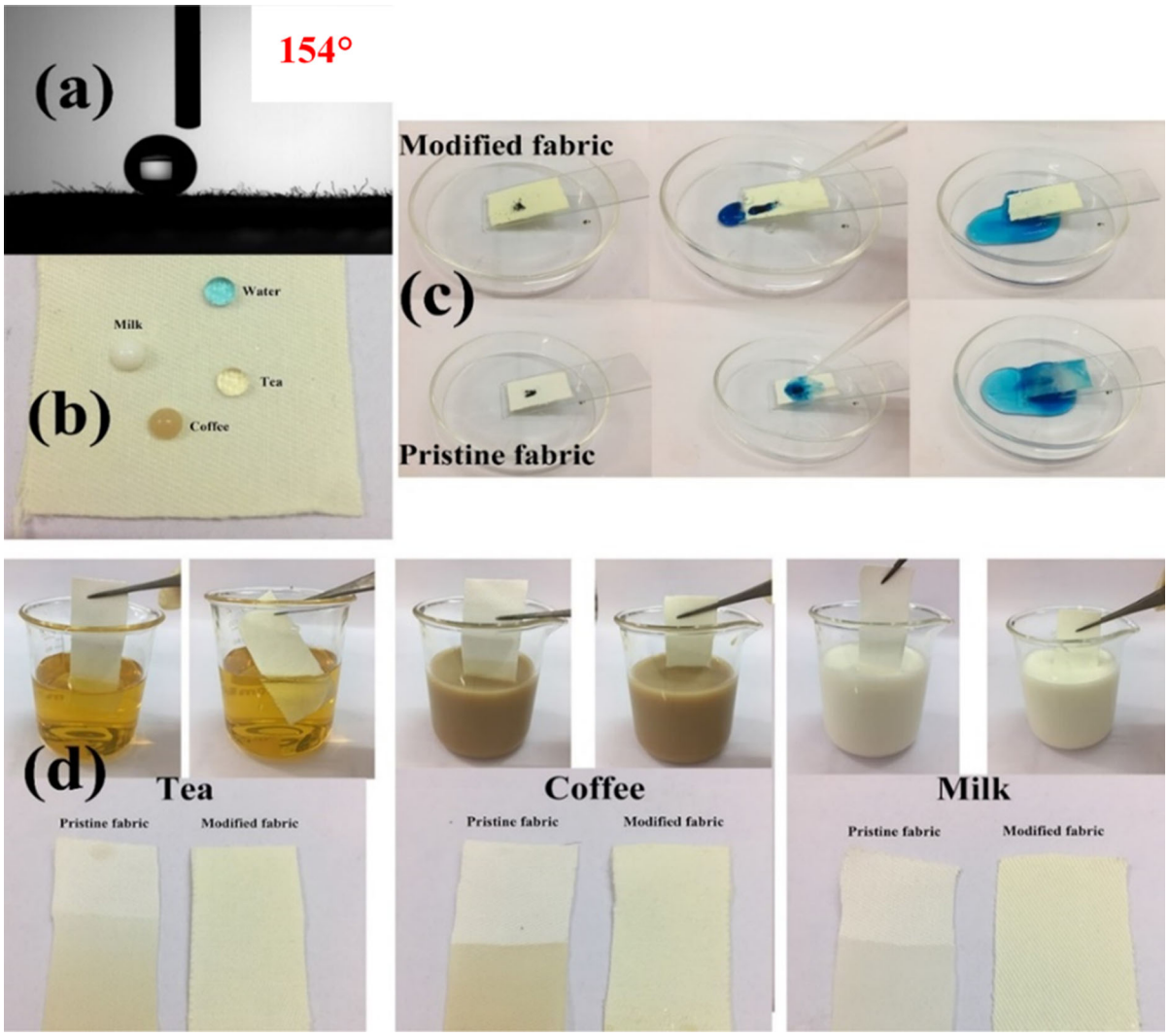


Fig. 6 Images of water droplet (**a**) and other liquid droplets (**b**) on the $(PEI\text{-}H/SiO_2)_3$@HDTMS fabric; Self-cleaning behavior (**c**) and anti-fouling property test (**d**) of pristine fabric and $(PEI\text{-}H/SiO_2)_3$@HDTMS fabric

Abrasion test

Figures 10 and 11 presented the changes of WCA and UV protection performance of $(PEI\text{-}H/SiO_2)_3$@-HDTMS fabric with abrasion times, respectively. As shown in Fig. 10, the WCA of the fabric did not show an obvious decline with the increasing abrasion times, remaining 151° after suffering 300 abrasion times. Additionally, the UPF value, T(UVA) and T(UVB) of $(PEI\text{-}H/SiO_2)_3$@HDTMS fabric before abrasion test were 686.13, 0.51% and 0.11%, respectively. As Fig. 10 showed, UPF value of the fabric was still greater than 400 after 300 abrasion times. According to the Australian/New Zealand standard, the fabric at this moment fully met the excellent UV protection rating. The results manifested that the fabric could withstand at least 300 abrasion times.

Other properties

To characterize the thickness of the coating, the thickness of the fabric before and after modification were measured. As shown in Table 4, the thickness of the fabric increased by 0.09 mm after modification which represented that the thickness of the coating was approximately 0.045 mm. Besides, the air

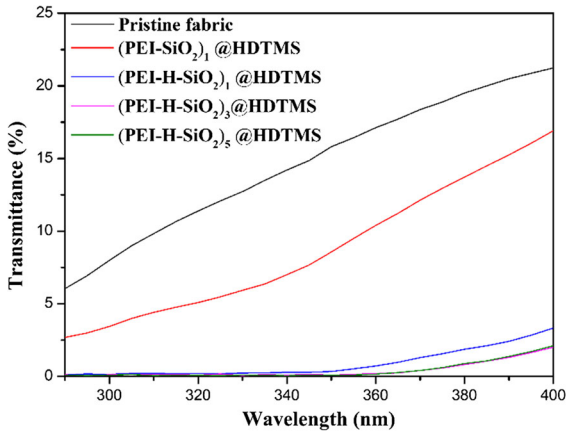


Fig. 7 Transmittance spectra of pristine and modified fabrics

permeability of modified fabric was 36.6 mm/s, decreasing by 16.7%. The little reduction was attributed to the silica nanoparticles and the HDTMS film which might cover the pores between the fibers. Nonetheless, the result indicated that the functional coating did not have a big impact on the air permeability of the cotton fabric. Furthermore, due to the flexibility of the polysiloxane chain formed by the polymerization of HDTMS, the bending rigidity of the modified fabric decreased, and thus the flexibility of the fabric improved.

According to the standard "Standard 100 by OEKO-TEX" (2018) (Environmental Textile Standard 100) developed by the International Environmental Textile Association, the safety of the obtained fabric was identified. Fabrics are divided into four categories: baby products (Class I), products that is direct contact with skin (Class II), products that is non-direct contact with skin products (Class III), and decorative materials (Class IV). The higher the class, the stricter the corresponding criteria.

The "Limited Values and Color Fastnesses" in Standard 100 by OEKO-TEX (2018) specifies the types and limited values of hazardous substances. It was found that no harmful substances listed in the appendix was used during the finishing process of the fabric. In order to further verify the safety of the

Table 1 UV resistance property of pristine and modified fabrics

Samples	T(UVA)%	T(UVB)%	UPF
Pristine fabric	15.02	8.16	9.80
$(PEI/SiO_2)_1$@HDTMS fabric	10.19	0.17	20.95
$(PEI\text{-}H/SiO_2)_1$@HDTMS fabric	1.08	0.11	390.67
$(PEI\text{-}H/SiO_2)_3$ @HDTMS fabric	0.51	0.11	686.63
$(PEI\text{-}H/SiO_2)_5$@HDTMS fabric	0.51	0.08	876.13

Table 2 UPF values of various UV-resistant cotton fabrics

Nos.	Method	UV protectant	UPF	Refs.
1	Pad-dry-cure	Graphene	500 +	Hu and Tian (2015)
2	LBL	Graphene oxide/chitosan	452.0 (10 layers)	Tian and Hu (2016)
3	LBL	Graphene doped PEDOT: PSS/chitosan	312.0 (6 layers)	Tian et al. (2016)
4	Pad-dry-cure	Nano-TiO_2	120.0	Chen et al. (2018)
5	Hydrothermal growth	ZnO@SiO_2 nanorod	101.5	Wang et al. (2011)
6	Pad-dry-cure	Nano-ZnO	150.0	Mai et al. (2018)
7	Hydrothermal growth	Flower-like TiO_2 particles	50 +	Huang et al. (2015)
8	LBL	ZnBDC	50 + (8 layers)	Lu et al. (2018)
9	In-situ synthesis	ZnO nanorod	50 +	Huang et al. (2019)
10	Pad-dry-steam	UV-DTHM	46.5	Shen et al. (2014)
11	Exhaustion method	New UV absorbers	140	Mamnicka and Czajkowski (2012)
12	LBL	FBA/PDDA	40 +	Wang and Hauser (2010)
13	LBL	PEI-H/SiO_2	800 + (5 layers)	Our study

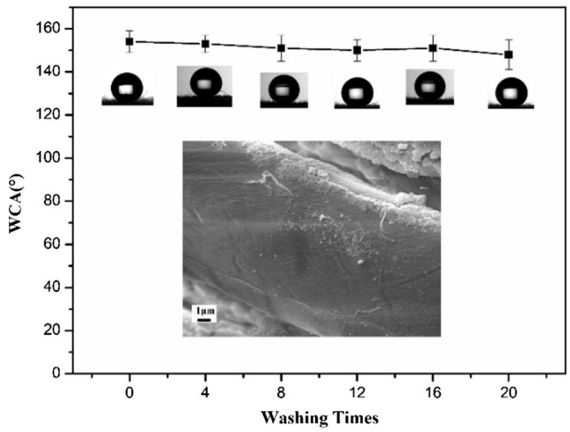


Fig. 8 WCA changes of the $(PEI\text{-}H/SiO_2)_3$@HDTMS fabric with washing times (inset was SEM image after 20 washing times)

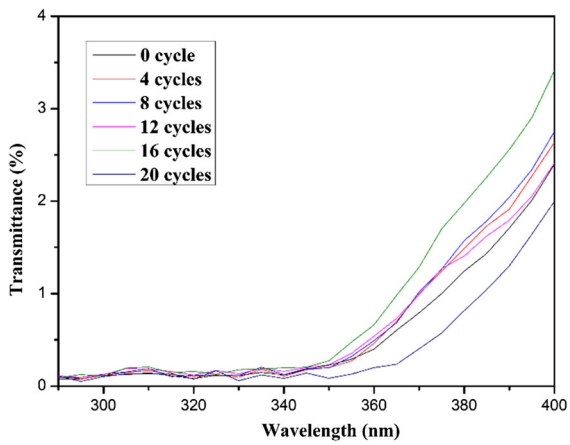


Fig. 9 UV transmittance spectra of modified fabrics after washing test

Table 3 UV resistance property of the modified fabrics after washing test

Washing times	T(UVA)%	T(UVB)%	UPF
0	0.51	0.11	686.63
4	0.72	0.10	620.34
8	0.82	0.12	545.14
12	0.86	0.13	517.97
16	0.80	0.14	478.75
20	1.09	0.14	427.67

obtained fabric, the formaldehyde content, pH value and the content of prohibited azo compounds were detected. As shown in Table 5, formaldehyde and

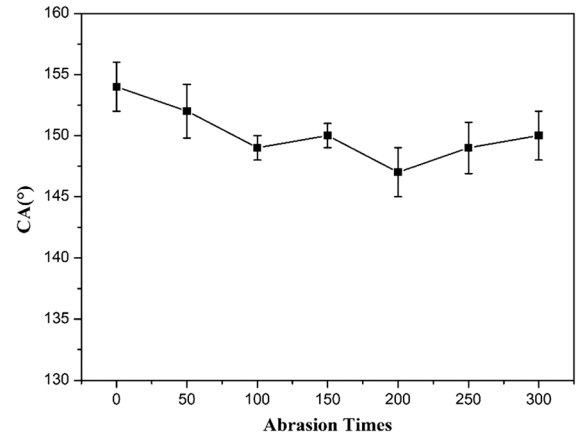


Fig. 10 WCA changes of the $(PEI\text{-}H/SiO_2)_3$@HDTMS fabric with abrasion times

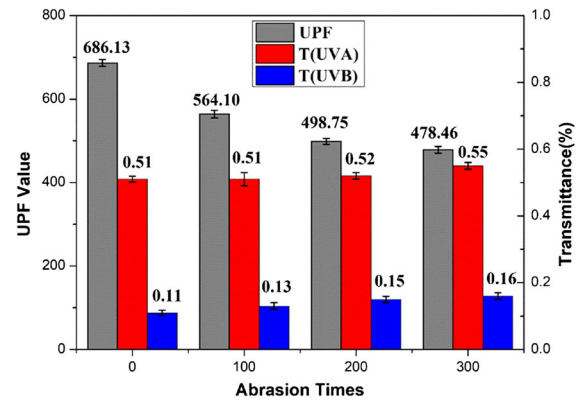


Fig. 11 The effect of abrasion times on UV protection performance of fabric

prohibited azo compound were not detected on the obtained fabric, and the pH value of the fabric was 6.7. All the above three indicators met the requirements for baby products (Class I) in the standard. Hence, the test results can well prove that the modified fabric is safe for human body and the environment. Besides, wet and dry crocking fastness are also provided in Table 5. The results showed that modified fabric possessed good fastness and also met the standard of Class I products.

Conclusion

In summary, this work provided a novel approach to fabricate robust UV-resistant and superhydrophobic coating upon cotton fabric by sequentially depositing

Table 4 Other properties of cotton fabrics

Sample	Thickness (mm)	Air permeability (mm/s)	Bending rigidity (mN cm)	
			Warp	Weft
Pristine fabric	0.41	43.9	8.98	3.89
(PEI-H/SiO_2)$_3$@HDTMS fabric	0.50	36.6	3.22	1.76

Table 5 Safety and crocking fastness of modified cotton fabric

Item	Standard value	Measured value	Judgement
Formaldehyde content (mg/kg)	Class I: not detected	Not detected	Qualified
pH value (extract liquor: 0.1 mol/L KCl solution)	Class I: 4.0–7.5	6.7	Qualified
Forbidden azo compounds	$\leq$ 20 mg/kg	Not detected	Qualified
Crocking fastness			
Wet	Class I $>$ 4	4–5	Qualified
Dry		4–5	

functionalized polyethyleneimine (PEI-H), SiO_2 and HDTMS via layer-by-layer assembly and dip-coating. Organic UV absorber (UV-0) was introduced to the surface of cotton fabric by grafting onto PEI. It was demonstrated that the cotton fabric was endowed with superior UV resistance performance with UPF value more than 800, resulting from the synergistic effect between organic UV absorber (UV-0) and inorganic UV shielding agent (SiO_2). Meanwhile, the cotton fabric not only possessed superhydrophobicty with a WCA of 154°, but also showed good self-cleaning and anti-fouling properties. Importantly, the multifunctional fabric exhibited outstanding durability against washing and abrasion test. Furthermore, the obtained fabric was safe for human body. The fabrication method is simple, fluorine-free and could achieve unique properties which make it available for application in outdoor field.

Compliance with ethical standards

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

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