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ORIGINAL RESEARCH

Hydrophobic, fireproof, UV-blocking and antibacterial cotton fabric activated by bio-based PA/ODA/TiO_2

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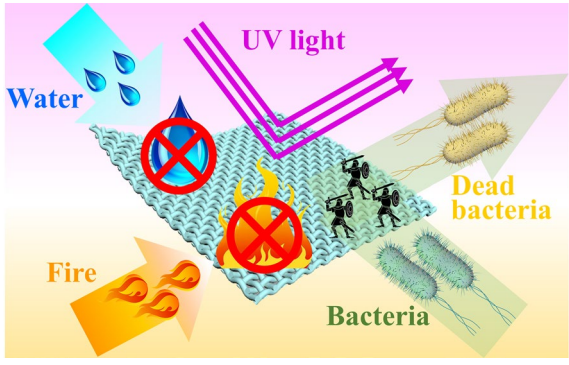
Abstract Versatile cotton fabrics can be used in a variety of special environments and offer unparalleled advantages in textile products. In this work, bio-based phytic acid (PA), octadecylamine (ODA) and TiO_2 (NPs) were used as raw materials to prepare multifunctional cotton fabrics with excellent flame retardant (LOI = 48.5%), hydrophobic (WCA = 152°), UV-blocking (UPF = 2000) and antibacterial (BR = 100%) properties through a facile and scalable dip coating and spraying process. Firstly, the phytic acid was grafted onto the surface of cotton fabric by esterification reaction between its phosphoric acid group and the hydroxyl group of cellulose molecules. Then ODA reacted with the residual phosphoric acid group of phytic acid to form an ODA layer, for further immobilizing TiO_2 (NPs) particles on the surface of cotton fabric. The resulting cotton fabric possessed excellent flame resistance (LOI > 36.2%), hydrophobicity (WCA > 138°), UV-blocking (UPF = 2000) and antibacterial abilities (BR > 96.0%) even after 20 washing cycles. Moreover, this modification process did not sacrifice the desired cotton properties, including water vapor permeability, flexibility and tensile strength. This work proposed a simple and scalable pad-dry curing method to construct stable and multifunctional cotton textiles, which have broadened application prospects in many fields.

Graphical abstract



Keywords Multifunctional cotton fabric · Bio-based · Surface modification · Phytic acid

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Introduction

Cotton fabrics are widely used in home decoration, clothing and technical textiles (Yetisen et al. 2016; Ahmed et al. 2020; Karim et al. 2020; Balasubramanian et al. 2021; Li et al. 2021) because of their wide sources, degradability, low cost, breathability, softness and wearing comfort (Flint 1950; Rowland et al. 1976; Park et al. 2004; Klemm et al. 2005). Unfortunately, they have some disadvantages, for example, their moisture-absorbing properties easily lead to the multiplication of bacteria on the surface. When a large number of microorganisms multiply, cross-infection, unpleasant odor and quality deterioration may occur (Zhou and Kan 2015; Cai et al. 2018; Duan et al. 2020; Gao et al. 2021; Wang et al. 2021). Cotton fabrics have a low limiting oxygen index and a low onset ignition temperature (360–425 °C), which make these materials highly flammable. When exposed to flame, cotton fabrics will burn quickly, emitting large amounts of heat and toxic fumes (Xu et al. 2019; Li et al. 2020; Chen et al. 2021). In addition, cotton fabrics also suffer from oxidation aging and performance degradation, when exposed to high UV intensity of the atmosphere for a long time. (Abidi et al. 2009; Yin et al. 2014; Liu et al. 2022a, b). Hence, it is vital to develop multifunctional cotton fabrics with hydrophobic, antibacterial, flame retardant and UV resistance properties to provide a safe environment for human beings.

Halogenated compounds have been the most effective and widely used flame retardants on cotton fabrics in the past decades. But halogenated flame retardants are gradually disappearing from research laboratories, due to their negative impact on the environment and health (Zaikov and Lomakin 2002). The use of renewable resources including nucleic acid (DNA), protein, phytic acid (PA) and other formaldehyde-free, halogen-free, environmentally friendly and efficient bio-based flame retardants has attracted widespread attention (Alongi et al. 2014; Qiu et al. 2018; Li et al. 2019; Miao et al. 2021; Wan et al. 2021; Sykam et al. 2021; Özer and Gaan 2022). For example, DNA coatings were constructed on cotton fabrics using a layer-by-layer technique, resulting in self-extinguishing properties and achieving a 28.0% limiting oxygen index (LOI) (Alongi et al. 2013). Nevertheless, the limited source of DNA hinders its large-scale application. By contrast, the amino acids in whey protein are mostly sulfur-containing amino acids, and casein is a phosphorylated protein. When the surface of cotton fabric was coated with whey protein or casein suspension, the burning rate of cotton fabric was reduced and the burning time was effectively increased (Alongi et al. 2013; Bosco et al. 2013; Faheem et al. 2019; Liu et al. 2020). However, it is difficult to endow cotton fabrics with self-extinguishing properties, due to insufficient content of flame retardance elements in these proteins. Phytic acid (PA), a natural molecule extracted from plant tissues such as grains and rapeseed, has been widely used for flame retardant fabrics, because of its environmental friendliness, biocompatibility and phosphorus-rich nature (one phytic acid molecule has six phosphate groups) (Li et al. 2019, 2020; Liu et al. 2019, 2020; Thota et al. 2019; Sykam et al. 2021). However, PA is limited in making flame retardant fabrics as it degrades cellulose by the acidic effect, resulting in a significant loss of strength in cotton fabrics.

Due to their polyhydroxy structure, cotton fabrics are prone to absorb water, which hinders their application in special fields (Zhou et al. 2018; Yang et al. 2021; Wang et al. 2022; Wu et al. 2022). Good hydrophobicity can reduce the surface contamination of cotton fabrics and facilitate high-value applications in special environments (Wang et al. 2014; Xu et al. 2020). The hydrophobic treatment of cotton fabric surfaces is achieved by a combination of reduced surface energy (Latthe et al. 2014) and surface roughening (Zou et al. 2013), which also has been applied to stain prevention (Xi et al. 2015), self-cleaning (Mishra and Butola 2018), anti-icing (Latthe et al. 2019) and oil–water separation (Zhou et al. 2019). The low surface energy of cotton fabrics is mainly achieved by grafting fluorinated compounds (Zhang et al. 2018) or polysiloxane polymers (Przybylak et al. 2016). However, most of these materials are made from non-renewable or even toxic raw materials and may have serious consequences for human health and the environment, thus running counter to sustainable development goals. Octadecylamine (ODA) can reduce the surface energy of cotton fabrics to achieve hydrophobicity, due to its extra-long alkane chain. (Yan et al. 2020; Lin and Lee 2021; Liu et al. 2022a, b). Moreover, ODA possesses the characteristics of low cost, wide source, degradability and biocompatibility, which have attracted great interest from researchers (Hu et al. 2022). Besides, the

micro/nano-structures on the fabric surface are mainly achieved by loading some inorganic nanomaterials, such as ZnO (Athauda et al. 2013), SiO_2 (Lin et al. 2018) and TiO_2 (Lee et al. 2013; Yang et al. 2018). Due to its UV absorption ability, TiO_2 is also widely used in functional textiles for realizing self-cleaning, antibacterial and UV protection properties (Wu and Long 2011; Yu et al. 2013; Shaheen et al. 2019; Raeisi et al. 2021; Sheng et al. 2021; Zhu et al. 2021). However, the weak interface bonding force between inorganic nanomaterials and textile fibers is a major challenge for the further application of TiO_2 (NPs).

In this work, we prepared multifunctional cotton fabrics with flame retardant, hydrophobic, UV-resistant and antibacterial properties based on low-cost and bio-based raw materials PA, ODA and TiO_2 (NPs). Flame retardant fabric P-CO was prepared by covalently grafting phytic acid onto the surface of cotton fabric through esterification reaction in phytic acid, urea and dicyandiamide system. Furthermore, TiO_2 (NPs) particles and ODA were deposited sequentially on the surface of P-CO fabrics by atomization technique. Meanwhile, ODA will react with the residual phosphoric acid group on the surface of P-CO fabrics via amide reaction and ODA layer was formed on its surface. At the same time, the TiO_2 (NPs) particles were firmly capsulated by ODA layer on the surface of cotton fabric. The synergistic effects of PA, ODA and TiO_2 endowed POT-CO fabrics with efficient flame retardant, hydrophobic, anti-UV and antibacterial properties. To demonstrate the relationship between structure and performance, the surface morphology and chemical structure of POT-CO fabrics were confirmed by SEM, ATR-FTIR, XPS and XRD, and the flame retardancy, hydrophobicity, UV resistance, antibacterial activity and durability of POT-CO fabrics were comprehensively evaluated. Finally, the effects of the modified process on the inherent properties of the original fabrics were also assessed carefully, including tensile strength, water vapor permeability, and flexibility.

Experimental section

Materials

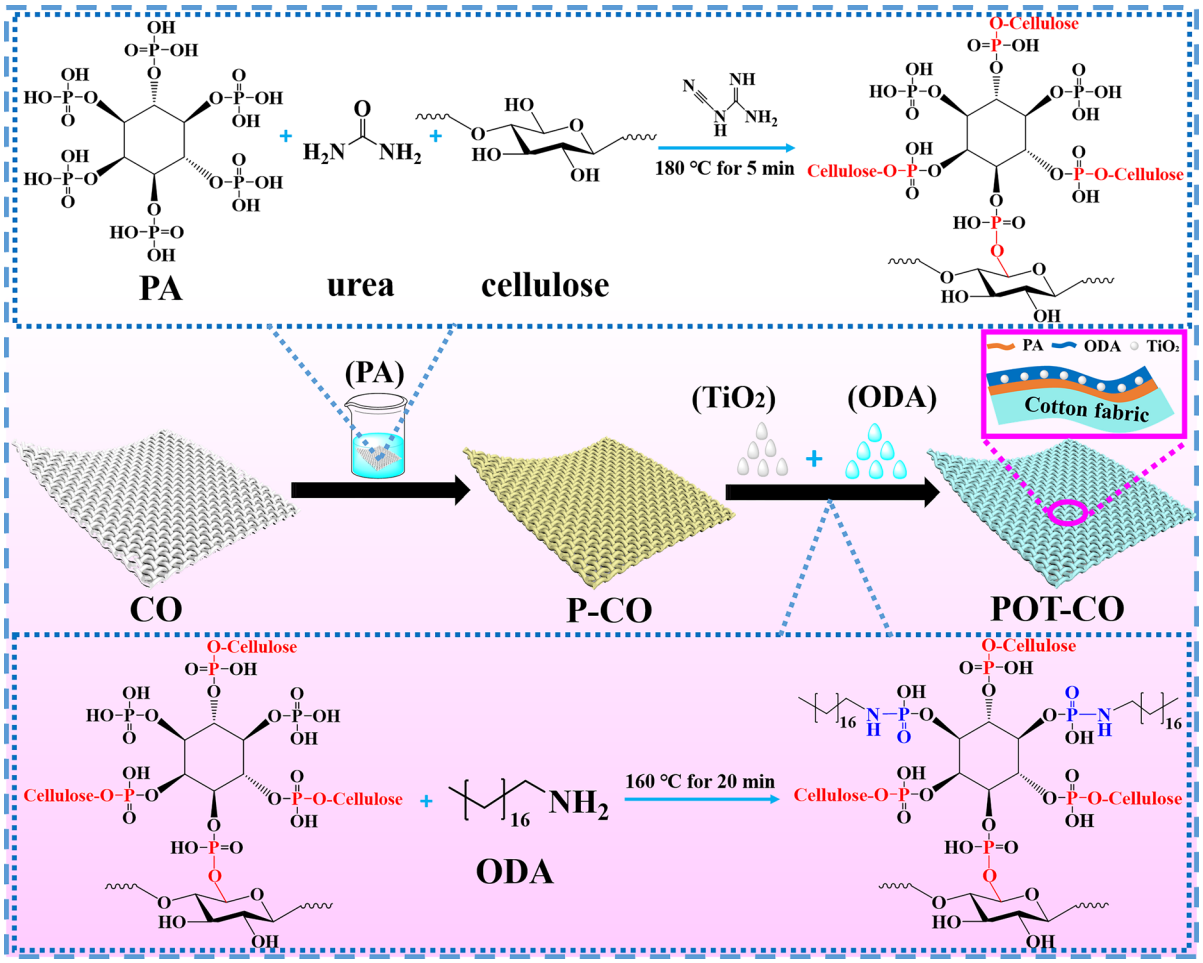
Cotton fabrics (CO, 120 g/m^2 weight) were purchased from Shaoxing Qi Dong Textile Co., Ltd (China). Before chemical modification, the cotton samples (5 cm × 5 cm, 4 pieces) were ultrasonically cleaned in a sodium lauryl sulfonate solution (100 mL, 2 wt%) for 60 min, washed with ethanol (100 mL, 95 wt%) for 30 min, and dried at 80 °C. Then, the cotton fabrics were dipped in a sodium hydroxide solution (100 mL, 1 wt%) at 90 °C for 60 min, washed with deionized water (100 mL, 3 times) and dried at 80 °C to obtain alkaline cotton fabrics which were used for further experiments. All reagents, including phytic acid (PA, 70 wt%), urea (AR, 99.0%), dicyandiamide (AR, 98.0%), NaOH (AR, 97.0%), ethanol absolute (AR, 99.5%), sodium lauryl sulfonate (AR, 98.0%), octadecylamine (ODA, AR, 99.8%) and TiO_2 (60 nm, 99.8%) were purchased from Shanghai Aladdin Co., Ltd (China) and used without further purification.

Preparation of modified cotton fabrics

Firstly, PA solution (0.3 mol/L, 100 mL) was prepared, and the urea (0.45 mol, 27.00 g) was dissolved in it to obtain finishing solution, while dicyandiamide (0.06 mol,

5.04 g) was added as catalyst. The alkaline cotton fabric was moved into the finishing solution at 70 °C for 60 min with a weight ratio of 1:20 ($W_{\text{cotton fabric}}$: $W_{\text{finishing solution}}$). Then, the cotton fabric was taken out, squeezed to control the wet absorption of the fabric at 120%, and baked at 180 °C for 5 min. Finally, the cotton fabric was washed with deionized water to remove the extra finishing solution and dried thoroughly in the oven at 80 °C to obtain P-CO fabrics. The crease recovery angle of CO and P-CO samples(Fig. S1a) and the pH change of washing leachate solution of P-CO samples (Fig. S1a) proves that the unreacted PA on the surface of P-CO fiber has been completely washed away.

TiO_2 nanoparticles were dispersed in ethanol and sonicated for 15 min to dispersed uniformly. Afterwards, the TiO_2 ethanol solution (10 mL, 1 wt%) was sprayed on P-CO fabric samples (5 × 5 cm, both sides) by an air-compression-type atomizer for 1 min and heated at 100 °C for 30 min. Octadecylamine ethanol solution (10 mL, 1 wt%, 3 wt%, 5 wt%) was prepared at 60 °C, and then the solution was sprayed on the cotton fabric samples (5 × 5 cm, both sides). The obtained cotton fabric samples in the previous step were experienced under an air-compression-type atomizer for 5 min and heated at 160 °C for 20 min.



Scheme 1 The preparation process of the POT CO fabrics

The final obtained samples were washed in ethanol (three times, 10 min each time) and dried at 80 °C for 2 h to obtain POT-CO-n fabrics (n represented the mass concentration of ODA), and the POT-CO-5 fabric sample with excellent comprehensive performance was used for all performance characterizations. The preparation process of the POT-CO fabrics is shown in Scheme 1.

For comparison, P-CO fabric loaded with ODA (PO-CO fabric) and P-CO fabric loaded with TiO_2 (PTCO fabric) were also prepared. PO-CO fabrics were obtained by spraying ODA ethanol solution (10 mL, 5 wt%) on P-CO fabrics for 5 min through an atomizer, followed by heating at 160 °C for 20 min. PT-CO fabrics were obtained by spraying TiO_2 ethanol solution (10 mL, 1 wt%) onto P-CO fabrics for 1 min by an atomizer, and then heated at 100 °C for 30 min. The final obtained samples were washed in ethanol (three times, 10 min each time) and dried at 80 °C for 2 h. Also, CO fabric loaded with ODA alone (ODA-CO fabric) and CO fabric loaded with ODA and TiO_2 (ODA/TiO TiO_2-CO fabric) were prepared, and the whole preparation process conditions were the same as above.

Characterizations

The chemical structures of control cotton fabric and modified cotton fabrics were evaluated by infrared spectroscopy (FTIR, Thermoelectric Corporation of America). The scanning range of the ATR-FTIR spectrometer was 4000–500 cm^{-1}. X-ray diffraction

(XRD) was performed in reflection mode on an X-ray diffractometer (Bruker AXS D8 Advance, Germany), and the 2θ ranged from 10° to 80° with a speed of 5°/min. XPS analysis was performed by an AXIS multifunctional X-ray photoelectron spectrometer (ULTRA DLD, Shimadzu Ltd., Japan) at a power of 450 W. Ultra-high resolution field emission scanning electron microscope (SEM, Zeiss, UK) with Energy Dispersive X-Ray Spectroscopy (EDX, Zeiss, UK) was used to observe the surface morphology of the fabric and the surface elemental composition before and after finishing. All samples (2 mm × 2 mm) were coated with gold before SEM testing and EDX was operated with a primary electron beam at an accelerating voltage of 2 kV. The thermal stability of the samples was determined by a thermogravimetric analyzer (TG, Netzsch, Germany) in the air and nitrogen atmosphere, respectively. After chopping the samples, of which 5–6 mg was prepared for testing in the range of 30–800 ℃ with a heating rate of 10 ℃/min.

The water vapor permeability, tensile strength, flexibility and washing durability of the fabric samples were carried out according to our previous reports (Wang et al. 2021; Xu et al. 2017, 2019). The test methods of the grafting rate (GR), hydrophobicity analysis, antibacterial property, flame retardant property and UV resistant property of the cotton fabrics were also introduced in the "Supporting information".

Results and discussion

Chemical structure of modified cotton fabrics

The control cotton fabric (CO) and the modified cotton fabric were characterized by FTIR, and the results are shown in Fig. 1a, b. Compared with the CO sample, the P-CO, PO-CO and POT-CO-5 fabrics displayed additional peaks at 1230 and 1056 cm^{-1}, which were attributed to the P=O and P–O–C stretching vibration (Ma et al. 2021), indicating that PA can be grafted on the cotton fabric surface by P(=O)–O–C bonds through the esterification reaction between the $-P=O(O\text{-}NH_4^+)_2$ group and the –OH group of cellulose (Liu et al. 2017; Xu et al. 2019). The band at 1719 cm^{-1} was attributed to C=O stretching vibration caused by the oxidation of PA during phosphorylation (Lu et al. 2018; Ma et al. 2021). Meanwhile, the new absorption peaks at 2923 and 2850 cm^{-1} of PO-CO fabrics and POT-CO-5 fabrics were corresponding to the CH_3 and CH_2 groups of ODA (Yan et al. 2020; Lin and Lee 2021), which indicated that ODA was grafted onto the cotton fabric by amide reaction with the phosphate group on P-CO fabrics. Furthermore, a new broad peak at 850–740 cm^{-1} in the POT-CO-5 fabric was attributed to the O–Ti–O bond (Pal et al. 2021; Rashid et al. 2022; Refaee et al. 2022), indicating the successful deposition of TiO_2 (NPs) on the surface of the cotton fabric.

XRD analysis was also carried out for the control cotton fabric and modified cotton fabric. As shown in Fig. 1c, the peaks at 2θ = 14.7°, 16.5°, 22.7°, and 34.3° were. typical peaks of crystalline structure of cellulose I, which appeared in the XRD spectra of both control cotton fabric and modified cotton fabrics (Xu et al. 2017, 2020; Duan et al. 2020), illustrating that the modification did not destroy the crystalline structure of cellulose. Compared to other samples, the characteristic peaks of TiO_2 at 2θ = 25.5° and 48.2° appeared in the POT-CO-5 fabrics (Shaheen et al. 2019; Sheng et al. 2021), which proved that the TiO_2 (NPs) were successfully deposited on the surface of the POT-CO-5 fabric. Furthermore, the increment in fabric weight also revealed the successful grafting of PA, TiO_2 (NPs) and ODA on the fabric surface, and the GR of POT-CO-5 fabric reached up to 8.5% (Fig. 1d).

To further confirm the chemical structure, the control cotton fabric and the treated cotton fabrics were analyzed by XPS and the results are shown in Fig. 2. From the wide-scan XPS survey spectra (Fig. 2a), new elements (N and P) appeared in all modified cotton fabrics compared to the CO sample, with the additional presence of Ti elements in the POT-CO-5 fabrics. Fig. 2b, c showed the high-resolution C 1s XPS spectra of CO and POT-CO-5, respectively. The former can be deconvoluted into three peaks at 288.05 eV (O–C–O), 286.40 eV (C–OH) and 284.80 eV (C–C/C–H), whereas the latter can be deconvoluted into two peaks at 286.32 eV (C–OH) and 284.50 eV (C–C/C–H) (Wang et al. 2021, 2022; Shen et al. 2022). To confirm the existence of covalent bonds between PA, ODA and cellulose chains of cotton fibers, high-resolution N 1s and P 2p XPS spectra of the POT-CO-5 fabrics were also analyzed. As shown in Fig. 2d, the N 1s peaks of POT-CO-5 fabrics appeared at 400.89, 399.87 and 398.58 eV, attributed to $–NH_2$, –NH– and –N= bonds (Yan

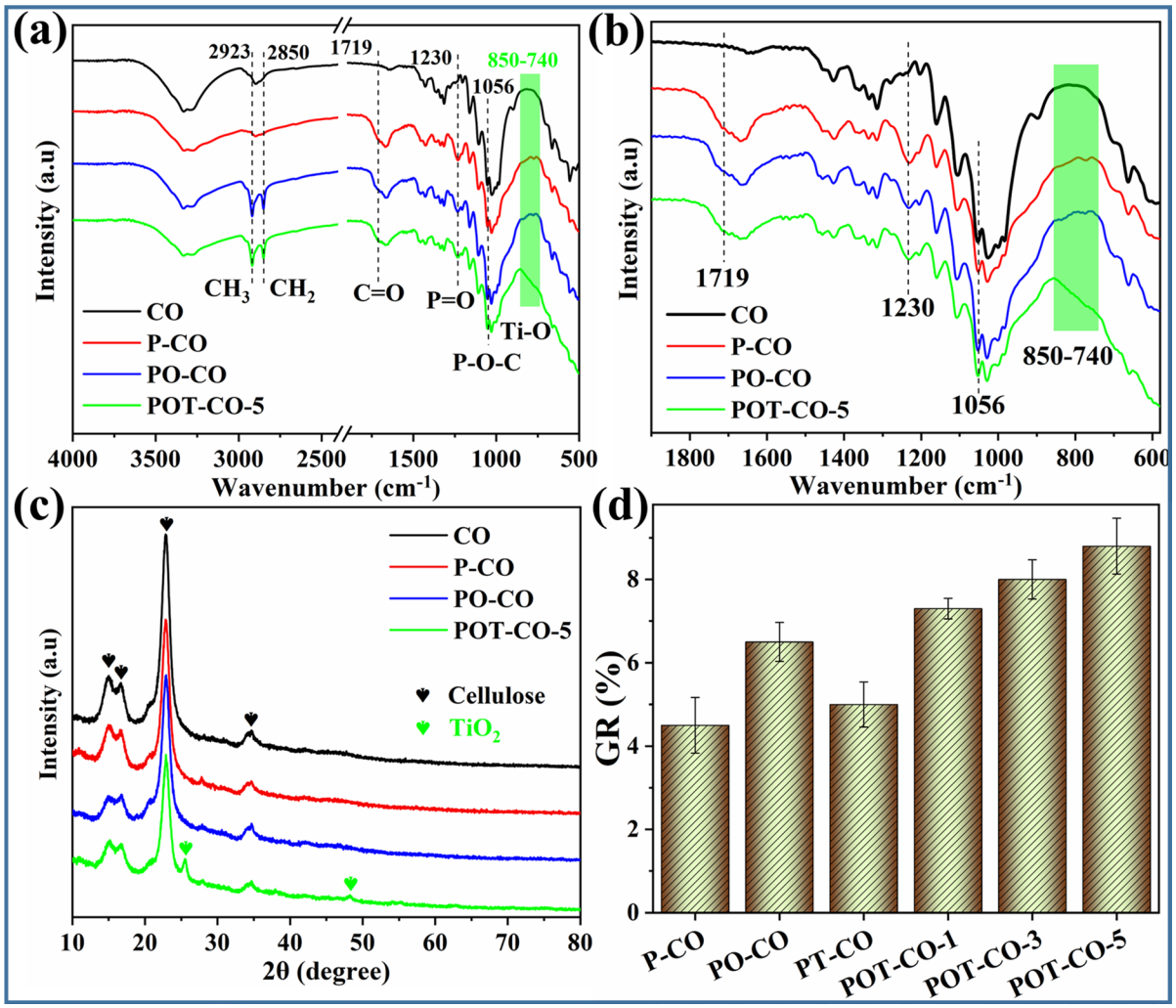


Fig. 1 ATR-FTIR (**a** and **b**)and XRD (**c**) spectra of CO, P-CO, PO-CO and POT-CO-5 fabrics; and the GR values of all samples (**d**)

et al. 2020; Lin and Lee 2021), respectively. The P 2p peaks of POT-CO-5 fabrics appeared at 134.32 and 133.38 eV (Fig. 2d), which was corresponding to P=O)–O–C bond between phytate and cellulose, and PO_2^{2-} for the unreacted –P=O(O–NH_4^+)$_2$ group (Liu et al. 2017; Xu et al. 2019; Ma et al. 2021). The high-resolution Ti 2p XPS spectra of POT-CO-5 fabrics were presented in Fig. 2f. The Ti 2p peaks of POT-CO-5 fabrics were deconvoluted at 465.00 and 457.00 eV, corresponding to the Ti $2p_{2/3}$ and Ti $2p_{1/2}$ bonds (Shaheen et al. 2019; Raeisi et al. 2021; Sheng et al. 2021), respectively, which proved the successful deposition of TiO_2 (NPs) on the POT-CO-5 fabrics surface. The element contents in the fiber surfaces were calculated based on these XPS results (Table S1). The data clearly demonstrated a significant difference between POT-CO-5 fabrics (78.59% C, 11.88% O, 2.55% N, 3.15% P and 3.84% Ti) and the control cotton fabric (54.63% C and 45.37% O). These XPS results suggested the successful grafting of PA, TiO_2 and ODA on the surface of cotton fabrics.

The surface morphologies of CO, P-CO, PO-CO, PT-CO and POT-CO-5 fabrics were characterized by SEM observation. As shown in Fig. 3a–c, it can be seen that the control cotton fabric exhibited a smooth and clear morphological structure as stated in previous reports (Xu et al. 2017, 2020; Wang et al. 2021,

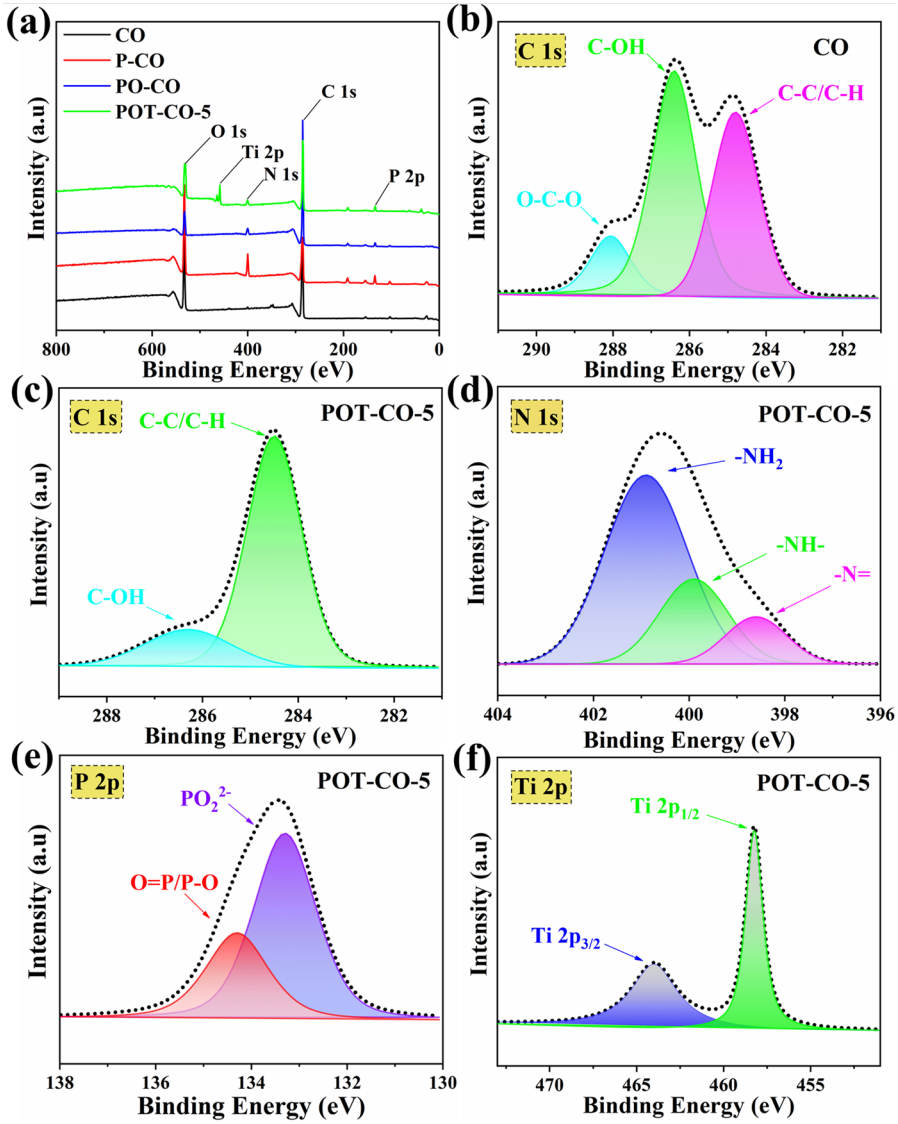


Fig. 2 XPS survey spectra of samples on wide range of all samples (**a**), and the deconvoluted C 1s XPS spectra of CO (**b**) and POT-CO-5 fabric (**c**), and the deconvoluted N 1s, P 2p, and Ti 2p XPS spectra of POT-CO-5 fabric (**d–f**)

2022). The surface of P-CO fabric was slightly rough (Fig. 3d–f) and a thin film appeared on the surface of PO-CO fabric (Fig. 3g–i), which can be attributed to the grafting coating of PA and ODA, respectively. It is worth noting that the surface of PT-CO fabric (Fig. 3j–l) was as smooth as the control cotton fabric, suggesting that the TiO_2 (NPs) have been washed off easily from the fiber surfaces. In contrast, many nanoparticles appeared on the surface of POT-CO-5 fabric (Fig. 3m–o), while the fiber surface was covered with a grainy thin film, which indicated the ODA layer successfully immobilized the TiO_2 (NPs) on the surface of POT-CO-5 fabric. In order to further analyze the surface structure of the modified cotton fabrics, EDS element mapping tests were performed on both the control and modified cotton fabrics (Fig. S2). Compared to the control cotton fabric, new elements N and P appeared on the P-CO, PO-CO and POT-CO-5 fabrics and were uniformly distributed on the surface of the cotton fabric. The N and P elements on the P-CO fabric were derived from urea and PA, and the N and P elements on the PO-CO and POT-CO-5 fabrics were derived from ODA, urea and PA. Furthermore, the additional presence of uniformly distributed Ti elements on the surface of POT-CO-5 fabric revealed the successful deposition of TiO_2

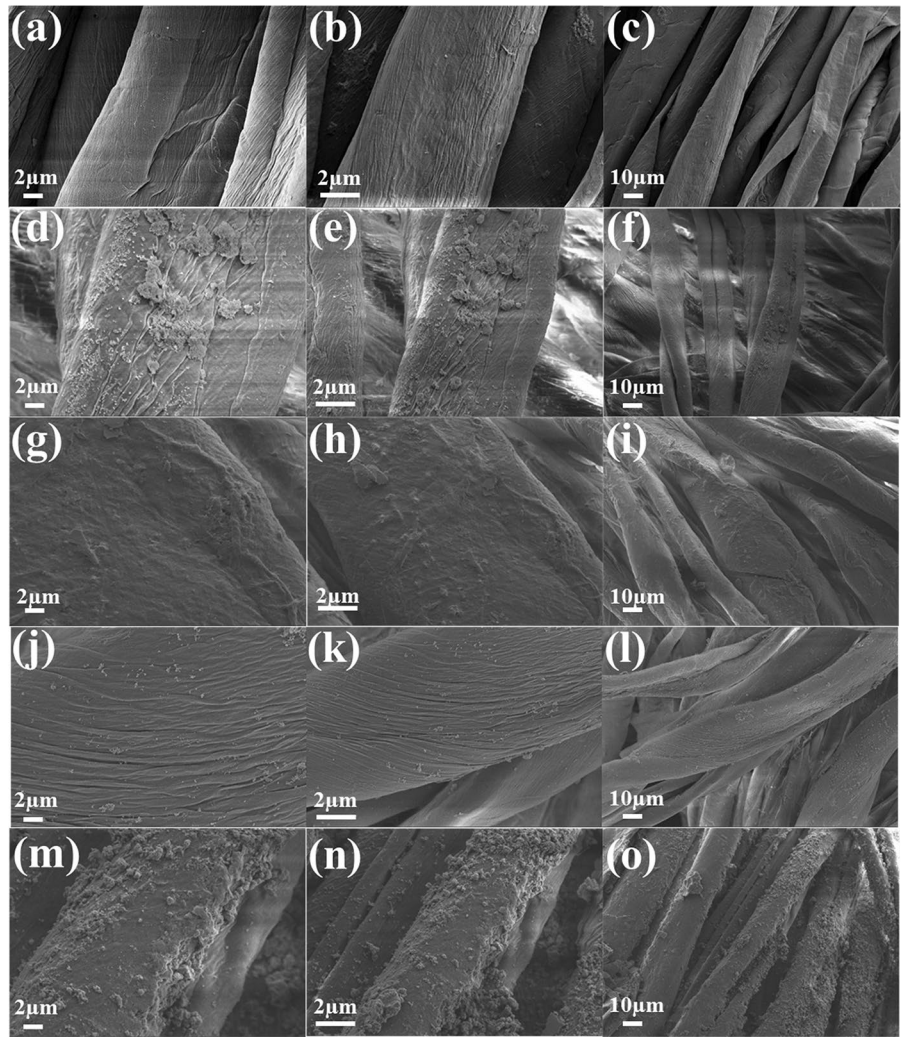


Fig. 3 SEM images of the fiber surface of CO (**a–c**), P-CO (**d–f**), PO-CO (**g–i**), PT-CO (**j–l**) and POT-CO-5 (**m–o**) fabrics

(NPs) on the surface of the modified cotton fabric. In conclusion, SEM and EDS provided strong evidence for the successful modification of cotton fabrics.

Water retardancy

The surface wettability of the modified cotton fabrics was studied by measuring the contact angle of a sessile water droplet on their surfaces. As shown in Fig. 4a–c, when the control cotton fabric was immersed in water, the control cotton fabric readily sank into the water and exhibited the hydrophilic properties of the conventional cotton fabric (Fig. 4d) (Xu et al. 2020). In contrast, when the POT-CO-5 fabric was immersed in water, the POT-CO-5 fabric exhibited water repellency and could float on the water surface (Fig. 4e–g), indicating that the modification of cotton fabric by ODA and TiO_2 (NPs) conferred hydrophobic properties (Fig. 4h). Another interesting comparison between control cotton fabric and POT-CO-5 fabric is shown in Fig. 4i, j. When droplets of various commonly used liquids (10 μL) were placed on the fabric samples, the droplets maintained a spherical shape on the surface of the POT-CO-5 fabric, meanwhile the droplets infiltrated into the control cotton fabric. Furthermore, as shown in Fig. 4k, the modified surface of POT-CO-5 fabric showed hydrophobic properties, while the unmodified surface showed hydrophilic properties, which indicated that the mist finishing technology endowed both sides of the modified fabric with different properties. Fig. 4l exhibited the contact angle of all samples, and

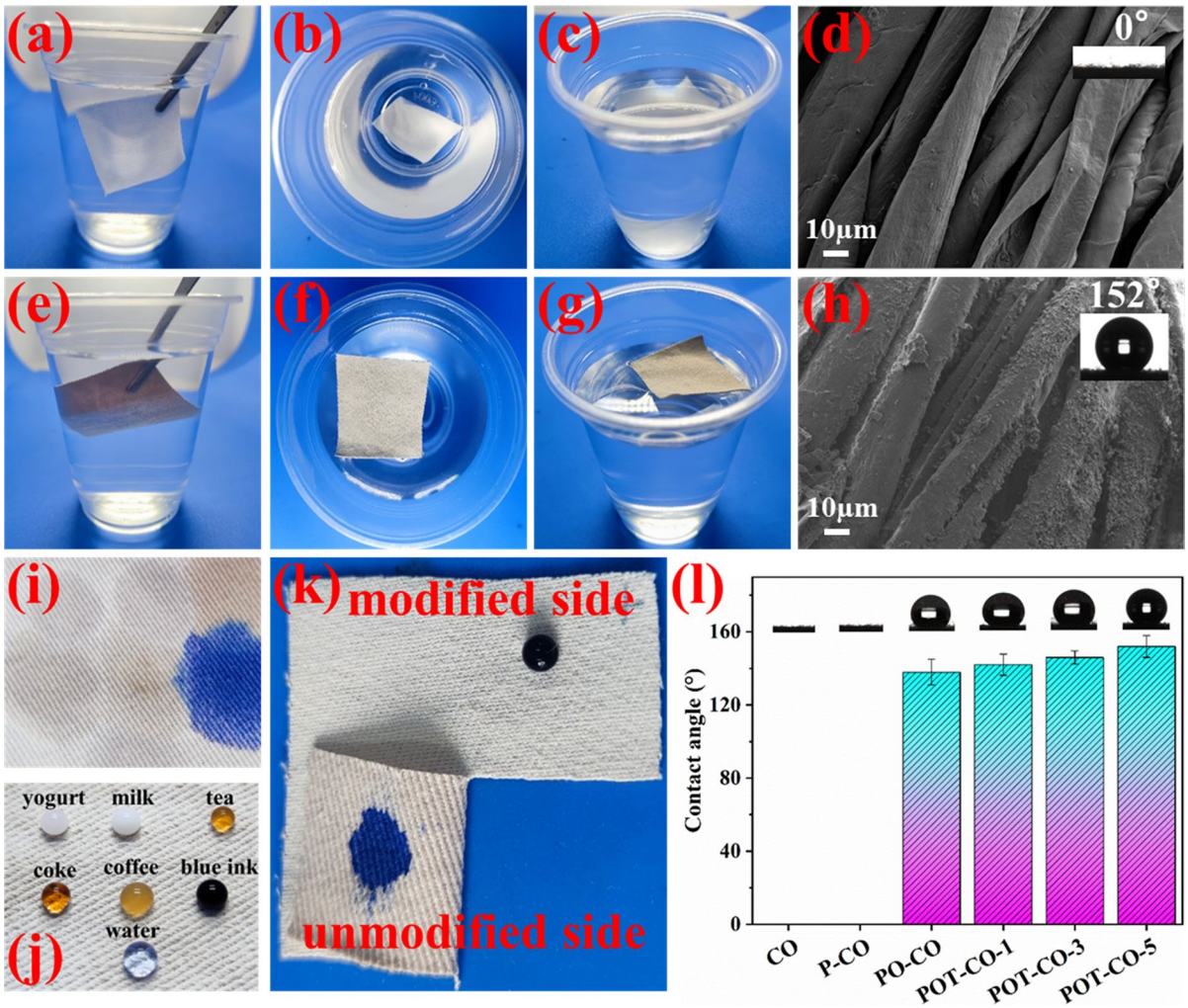


Fig. 4 Optical images of CO (**a–c**) and POT-CO-5 (**e–g**) fabrics on water surface. SEM images of CO (**d**) and POT-CO-5 (**h**) fabrics. Photographs of various solution droplets (10 μL) on CO (**i**) and POT-CO-5 (**j**) fabrics. Optical image of modified side and unmodified side of POT-CO-5 fabric (**k**). Contact angle of all samples (**l**)

the POT-CO-5 fabric showed superhydrophobic property, the contact angle of which reached 152°. Hence, the modified cotton fabrics realized good water repellency, which have potential for application in antifouling fabric.

We also observed the self-cleaning ability of the modified cotton fabric. As shown in Fig. 5a–c, the control cotton fabric rapidly absorbed the dye solution and was permeated by the contaminated solution, after immersing in a colored aqueous solution of blue ink. However, the POT-CO-5 fabric maintained a clean surface after immersion in the effluent (Fig. 5d–f). In another experiment, methyl orange (MO) powder was used to simulate the dust on the surface of the fabrics. When MO adhered to the fabric samples and they were rinsed with water droplets, there were significant differences between the control cotton fabric and POT-CO-5 fabric samples. As shown in Fig. 5g–i, the control cotton fabric was immediately wetted and contaminated with MO powder, even when rinsed with a large amount of water. In contrast, on the POT-CO-5 fabric, the fluid water carried away the MO powder quickly, showing a clean surface (Fig. 5j–l). These results indicate that the POT-CO-5 fabrics have excellent stain resistance and can be used in self-cleaning situations such as

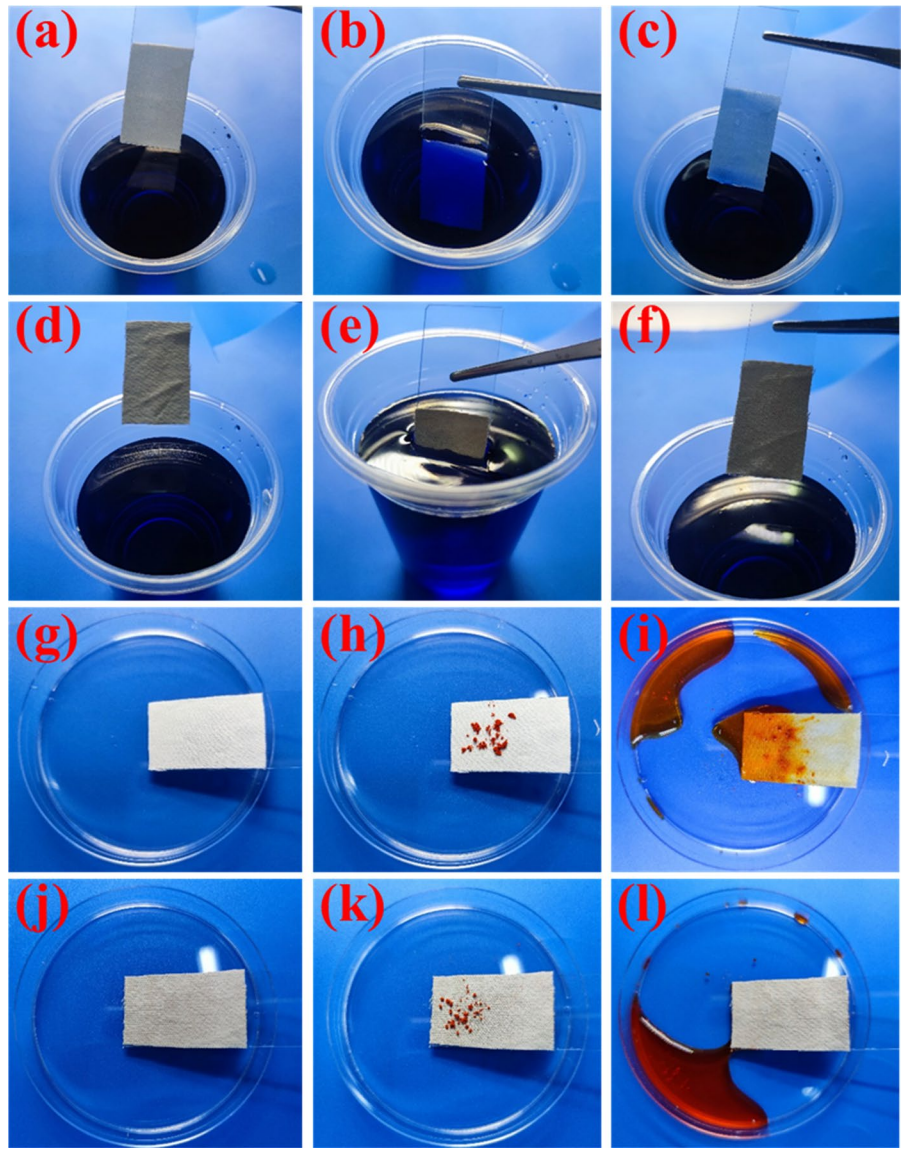


Fig. 5 Self-cleaning ability of CO (**a–c**) and POT-CO-5 (**d–f**) fabrics in polluted solutions. The self-cleaning behavior of the contaminated fabrics: the CO fabric (**g–i**) and POT-CO-5 fabric (**j–l**)

homes, industrial activities and outdoor decoration. Moreover, the POT-CO-5 fabrics also have a certain photocatalytic degradation ability because of the TiO_2 (NPs) fixed on the surfaces (Chimeh et al 2013; Chimeh and Montazer 2015). By placing the POT-CO-5 fabrics under UV irradiation, TiO_2 (NPs) on the surface of POT-CO-5 fabrics will degrade the dye molecules to achieve a self-cleaning ability (Fig. S3).

We also tested the contact angles of the POT-CO fabrics after exposuring to daylight simulator (a cabinet equipped with a UVC 4P SE tube lamp, T5 15W G13) for different times (Razaghpour et al. 2022), and the results were shown in Fig.S4. There was a negligible change in the contact angles of the POT-CO fabrics after UV-lighting. Interestingly, the contact angle undergoes a small decrease with the light exposure time increasing, which is attributed to the certain photocatalytic degradation ability of the TiO_2 (NPs) that affects the stability of the ODA coating on the fiber surface to some extent.

Flame retardant behavior analysis

Vertical burn test and LOI measurements were performed to evaluate the flame resistance of control cotton fabric and modified cotton fabrics. Fig. 6a, b

showed the combustion process of the control cotton fabric and POT-CO-5 fabric in the vertical burn test, and possible flame-retardancy mechanism of POT-CO-5 fabric. It was evident that when the control cotton fabric was exposed to the flame for only 1s, it burned strongly, quickly and completely, leaving only a small char residue. In contrast, POT-CO-5 fabric could not be ignited in the vertical burn test, even when exposed to the flame for 12s, and produced large amounts of char (char length = 3.0 cm) in the ignition area. The LOI values of all samples were shown in Fig. 7a, compared to the CO sample (LOI = 18.0%), POT-CO-5 showed excellent flame resistance (LOI = 48.5%) and much higher than previous reported cellulose-based materials treated by PA or other flame retardants (Fig. 7b; Table S2).

Subsequently, CO sample and POT-CO-5 fabric were tested by microscale combustibility calorimetry (MCC) to further evaluate the combustion and heat release processes. The lower heat release during combustion may reduce harm to people wearing fabrics made from modified cotton, and it may also protect the material underneath the fabric from heat (Chen et al. 2021; Miao et al. 2021). The heat release rate (HRR) of CO sample and POT-CO-5 fabric are shown in Fig. 7c. From the HRR curve we can see the obvious difference between CO sample and POT cotton fabric, compared to the peak of HRR (PHRR) − 287.56 W/g for CO sample, the PHRR of POT-CO-5 fabric is only 31.45 W/g, which is decreased by 89.06%. The difference in HRR between the control cotton fabric and the modified cotton fabric may originate from the fact that the phytate groups in the modified cotton fabric produce dehydrating agents such as polyphosphoric acid and phosphate during pyrolysis, thus accelerating the dehydration/carbonation and heat release from the cotton fiber, resulting in a lower temperature of peak HRR (Liu et al. 2017; Xu et al. 2019; Ma et al. 2021). Moreover, the fiber morphology of POT-CO-5 fabric before and after VFT was also measured by SEM. As shown in Fig. 7d–i, the overall woven structure of POT-CO-5 fabric remained intact after VFT, which indicated that PA could promote the dehydration and carbonization of cellulose to achieve flame retardant effect.

The results of vertical burn test, LOI and microscale combustibility calorimetry tests showed that the flame retardancy of cotton fabrics was significantly

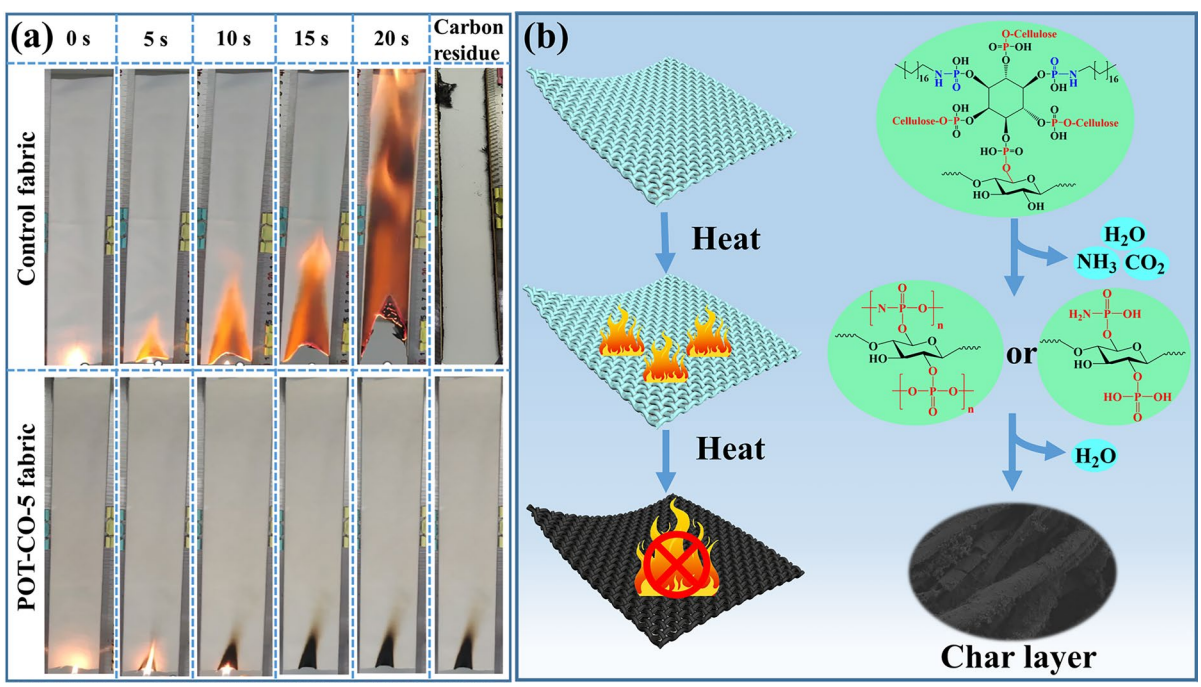


Fig. 6 Images during VFT of control cotton fabric and POT-CO-5 fabric (**a**), and possible flame-retardancy mechanism of POT-CO-5 fabric (**b**)

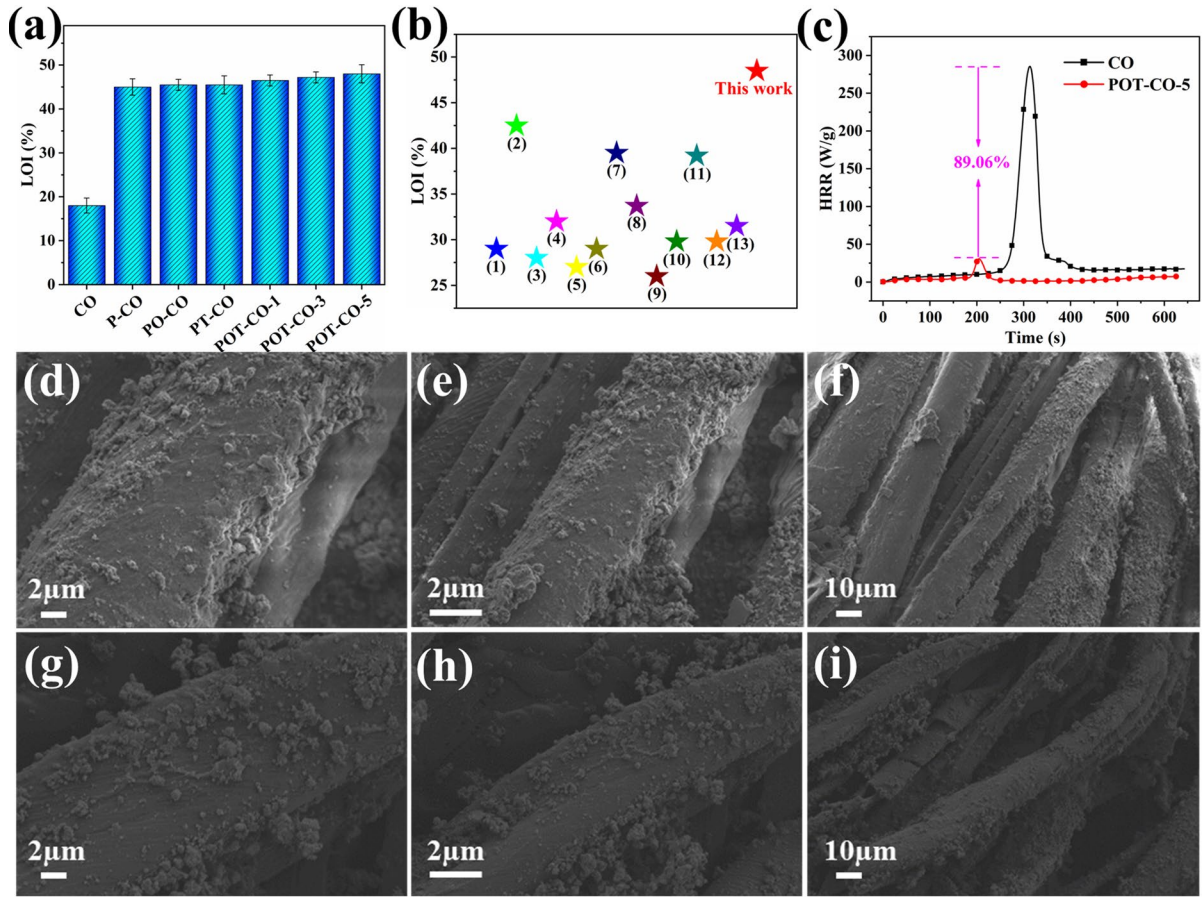


Fig. 7 LOI values of all samples (**a**); comparison on LOI values from other literature reports with this work (**b**); HRR as function of time for CO and POT-CO-5 fabrics (**c**); SEM images of POT-CO-5 fabrics before (**d–f**) and after (**g–i**) VFT test

improved via impeding combustion and promoting carbonization.

The thermal degradation properties of control and modified cotton fabrics were evaluated by TG and derived thermogravimetric (DTG) in N_2 and air atmospheres (Fig. 8). The corresponding data obtained from the TG and DTG curves are shown in Table 1, including 90% ($T_{10\%}$) mass retention temperature, maximum rate degradation temperature (T_{max}), maximum decomposition rate (V_{max}) and char residue at 800 °C. The $T_{10\%}$ of the control cotton fabric in a N_2 atmosphere was 343.0 °C. The main pyrolysis phase occurred in the range of 300.5–400.3 °C, and V_{max} was 2.6%/°C at 372.7 °C (T_{max}). The main pyrolysis phase of the control cotton fabric corresponded to the depolymerization of cellulose to form flammable gases, volatile liquids and solid residues, and finally at 800 °C retained 0.9% of the residue. Compared to the control cotton fabric, both $T_{10\%}$ (243.2 °C) and T_{max} (284.0 °C) of the POT-CO-5 fabric were significantly reduced, with the main pyrolysis phase occurred in the range of 209.0–298.5 °C, and the char residue at 800 °C increased to 36.5%. Phytic acid is rich in phosphorus and hydroxyl groups, which may produce phosphoric acid and polyphosphoric acid during thermal degradation. The derived phosphoric acid and polyphosphoric acid can promote catalysis, dehydration and carbonization of cellulose, inhibiting the production of levoglucan and leading to the formation of more protective layers of residual carbon (Cheng et al. 2020; Zhou et al. 2020; Ma et al. 2021). The formed carbon residue will impede heat transfer, formation and diffusion of volatiles,

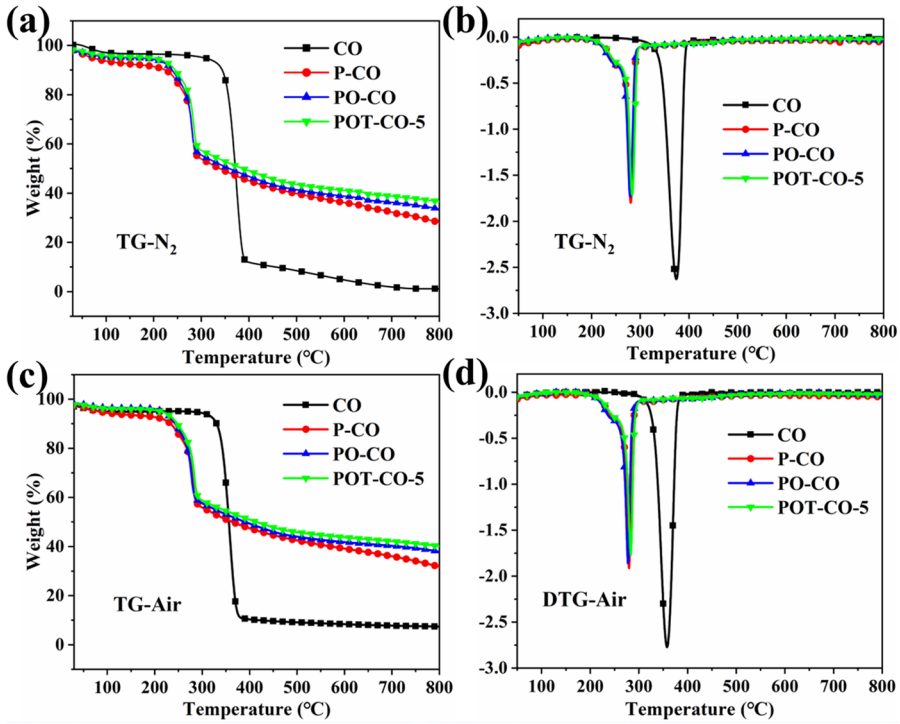


Fig. 8 TG and DTG curves of cotton samples in N_2 and air

Table 1 TGA data for cotton samples in air and N_2 atmospheres

Atmosphere	Samples	$T_{10\%}$ (°C)	T_{max} (°C)	V_{max} (%/°C)	Residue at 800 °C (%)
Air	CO	335.8	357.8	2.8	10.3
	P-CO	243.5	280.2	1.9	34.2
	PO-CO	249.1	277.3	1.8	39.4
	POT-CO-5	246.8	283.1	1.8	40.3
N_2	CO	343.0	372.7	2.6	0.9
	P-CO	230.0	280.2	1.8	29.5
	PO-CO	243.0	279.1	1.7	34.1
	POT-CO-5	243.2	284.0	1.7	36.5

resulting in a flame resistance effect for fabrics. Meanwhile, urea and ODA-treated modified cotton fabrics contain certain N elements, which enable the modified cotton fabrics to release inert gases such as NH_3 and N_2 during combustion, thus preventing the transfer of heat, flame and oxygen. Fig. 8c, d show the thermal oxidation stability of the fabrics in air atmosphere. The thermal degradation behavior of the control cotton fabric in air atmosphere was similar to that in nitrogen atmosphere, with the main thermal decomposition phase occurring from 295.7 to 393.5 °C. The $T_{10\%}$, T_{max} and V_{max} were 335.8 °C, 357.8 °C and 2.8%/°C, respectively, and the coke residual at 800 °C was 10.3%. Similarly, the decomposition temperature of POT-CO-5 fabric was reduced and the main thermal decomposition stage occurred between 200.3 and 299.3 °C. The $T_{10\%}$, T_{max} and V_{max} were 246.8 °C, 283.1 °C and 1.8%/°C, respectively, and the coke residue rate at 800 °C was 40.3%. In conclusion, an earlier initial decomposition occurs at lower temperature, which is ascribed to the deposition of PA. The phosphoric acid and polyphosphoric acid derived from PA promotes char residue generation, inhibiting heat and

mass transfer. These characteristics lead to the modified cotton fabrics possessing excellent thermal oxidation stability and flame resistance.

UV resistance of the modified cotton fabrics

Figure 9 shows the UV transmittance spectra and UPF values of the CO, P-CO, PO- CO, PT-CO and POT-CO-5 fabrics. As shown in Fig. 9, the CO sample shows a higher transmittance and a lower UPF value (UPF = 37.91) with UV transmittance of 2.21% and 2.52% for UVA and UVB, respectively. This means that UV can easily penetrate through CO samples, resulting in insufficient UV protection of cotton fabrics for human health (Shaheen et al. 2019; Raeisi et al. 2021). In contrast, P-CO, PO-CO, PT-CO and POT-CO-5 fabrics show excellent UV shielding properties, and the UPF values are significantly increased to 657.12, 1463.42, 868.96 and 2000, respectively, while all have low UVA and UVB transmittance (0.05%). PA is a kind of natural antioxidant which imparts UV resistance to the modified cotton fabric (Diouf-Lewis et al. 2017; Kirschweng et al. 2017; Li et al. 2022). Moreover, the UV absorption of TiO_2 is carried out by electron leap, and the absorption wavelength of UV light is equal to or less than the wavelength of TiO_2 band gap. When TiO_2 is exposed to incident light, it absorbs photon energy, allowing the valence band electrons of low energy to cross the band gap into the conduction band of high energy (Wu et al. 2021; Rashid et al. 2022). Therefore, with the synergistic effect of PA and TiO_2, POT-CO-5 fabric exhibits excellent UV protection ability (UPF = 2000, UVA = 0.05%, UVB = 0.05%).

Antibacterial effects of the modified cotton fabrics

Figure 10 showed the antibacterial activity of modified cotton fabrics against *E. coli* and *S. aureus*. All modified cotton fabrics showed excellent antimicrobial activity compared to the control cotton fabrics. The bacterial inhibition rates (BR) of P-CO and PO-CO fabrics against *E. coli* and *S. aureus* were 93.6% and 89.6%, 96.8% and 91.6%, respectively. This is due to the strong acidity of phytic acid, which endows the modified cotton fabrics with antibacterial properties (Li et al. 2021). It is noteworthy that POT-CO-5 fabric achieved 100% antibacterial rate against both *E. coli* and *S. aureus*. The antibacterial activity, reflected in the fact that

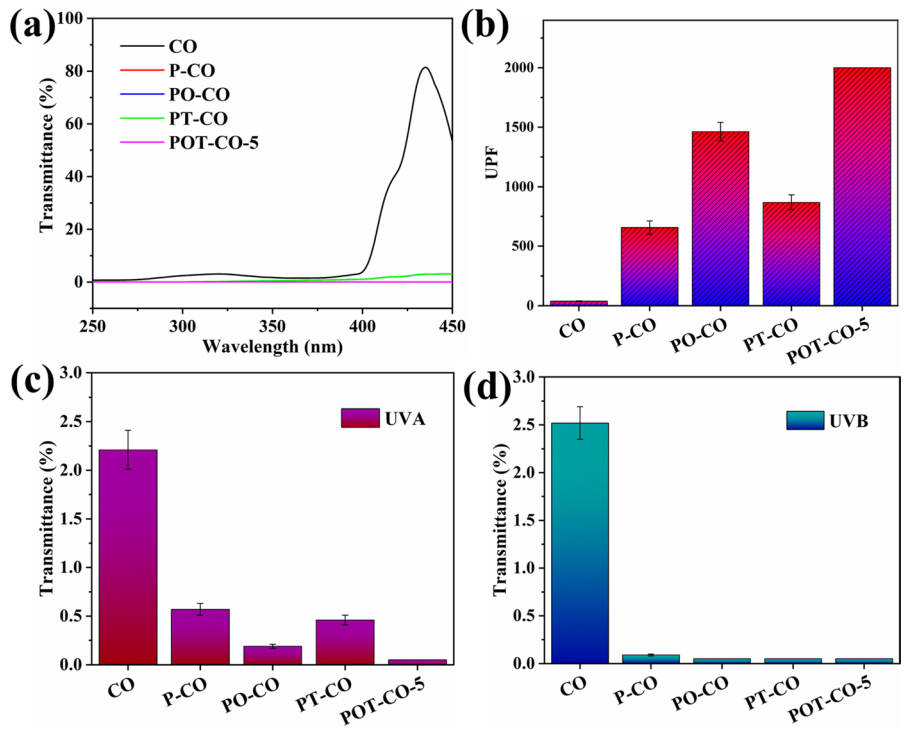


Fig. 9 Transmittance curves (**a**), UPF (**b**), UVA (**c**) and UVB (**d**) value of the CO, P-CO, PO-CO, PT-CO and POT-CO-5 fabrics

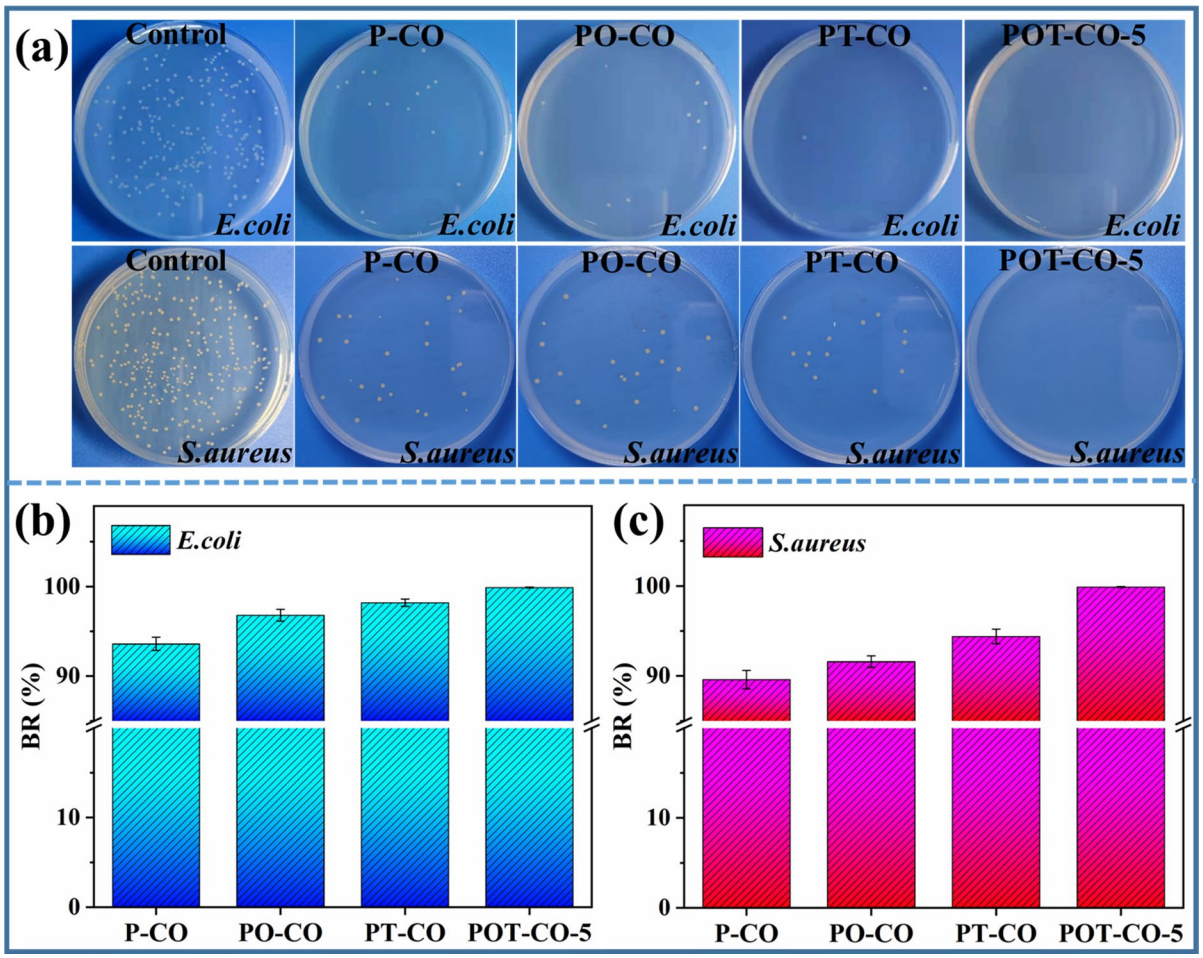


Fig. 10 Optical images of the antibacterial tests of control cotton fabric and the modified fabrics (**a**), statistical results of BR values of *E. coli* (**b**) and *S. aureus* (**c**)

TiO_2 can generate ROS, including bactericidal $OH^{\cdot}$ radicals, on its surface under photocatalysis (Sheng et al. 2021; Liu et al. 2022a, b). The synergistic effect with phytic acid at the same time resulted in POT-CO-5 fabric possessing excellent antibacterial properties. Moreover, the inhibition rates of PT-CO fabric against *E. coli* and *S. aureus* were only 98.2 and 94.4%, which were lower than those of POT-CO-5 fabric, indicating that the physically coated TiO_2 on P-CO fabric could be easily washed off by deionized water. Comprehensively, the POT- CO-5 samples showed superior hydrophobic, fireproof, UV-blocking and antibacterial effects among all samples (Table S3).

Washing fastness of the modified cotton fabrics

As shown in Fig. 11, the durability of the POT-CO-5 fabric for flame retardancy, hydrophobicity, UV resistance, and antimicrobial resistance was evaluated after multiple washing cycles according to the ISO 105-C10 standard method. As shown in Fig. 11a, the LOI of POT-CO-5 fabric was above 36.2% even after 20 washing cycles, and it also showed remarkable fire-retardant property with a self-extinguishing effect by vertical combustion test. Moreover, the water contact angle of POT-CO-5 fabric remained 136°, the UV resistance of UPF value kept at 2000, and the BR rate against both *E. coli* and *S. aureus* maintained above 96.0%. These data showed that POT-CO-5

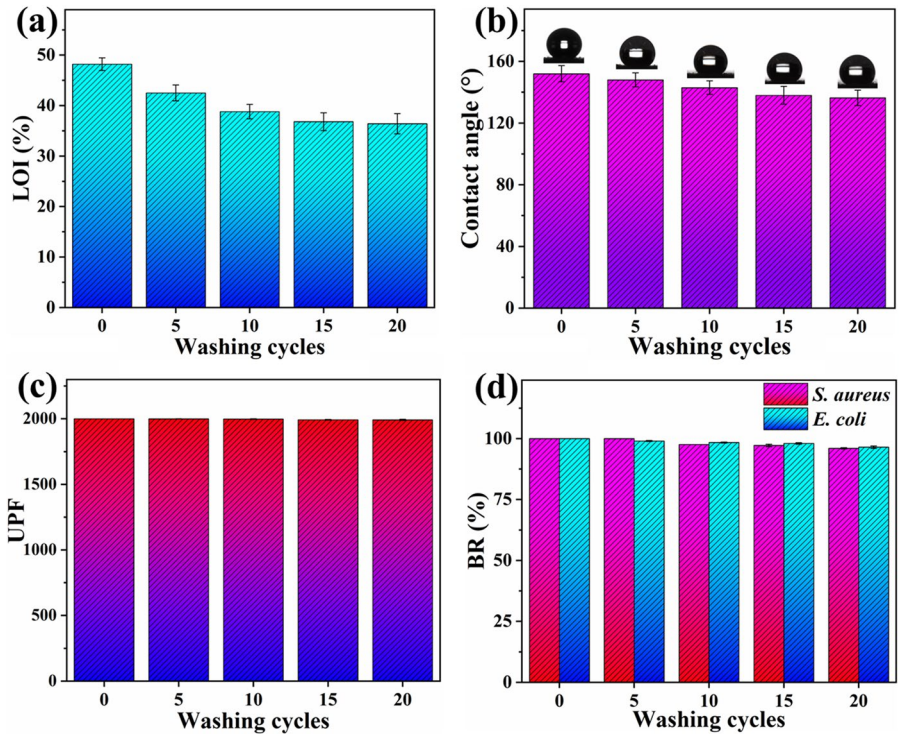


Fig. 11 LOI (**a**), contact angle (**b**), UPF value (**c**) and BR (**d**) of POT-CO-5 fabric after washing resistance test

fabric still maintains excellent flame retardant, hydrophobic, anti-UV and antibacterial properties even after 20 washing cycles.

Inherent properties of modified cotton fabrics

Good water vapor permeability, mechanical property, flexibility, and color are the signature features of cotton fabrics. Hence, the corresponding inherent properties of the modified cotton fabrics were tested, and the results were summarized in Fig. 12a–d. As shown in Fig. 12a, normal fluctuations of water vapor permeability were observed when compared the modified fabrics to the CO sample, and the fluctuation range was within the range of the error bar. So, the modification process had rarely impact on the breathability of cotton fabrics. Interestingly, the principle that hydrochloric acid meets ammonia gas to produce white particles was also used for proving the breathability of cotton fabrics. As showed in Fig. 12b, two bottles containing hydrochloric acid. and ammonia respectively were placed next to each other. The bottle containing ammonia was packaged with cotton fabrics (CO fabric and POT-CO-5 fabric), and the bottlecontaining hydrochloric acid was sealed with cap. When the cap of bottle was removed, both had a large amount of white smoke produced, revealing the breathability of the CO fabric and POT-CO-5 fabric. The tensile strength of different modified samples was slightly reduced compared to the CO sample (Fig. 12c). While the POT-CO-5 fabric still had a high strength retention (about 80%), which was sufficient to satisfy the application of the textile fabric. Moreover, there was no significant difference in the maximum loop height between the CO sample and the modified fabrics (Fig. 12d), indicating that their fabric flexibilities were comparable. Interestingly, our modification process shows insignificant color changes on fabric, as shown in Fig. S5. These results demonstrate that the modification process gave an insignificant impact on the desired features of cotton fabric.

Conclusions

In this work, versatile cotton fabrics with excellent flame retardant, hydrophobic, UV-blocking and antibacterial properties were constructed through a simple and scalable pad-dry curing

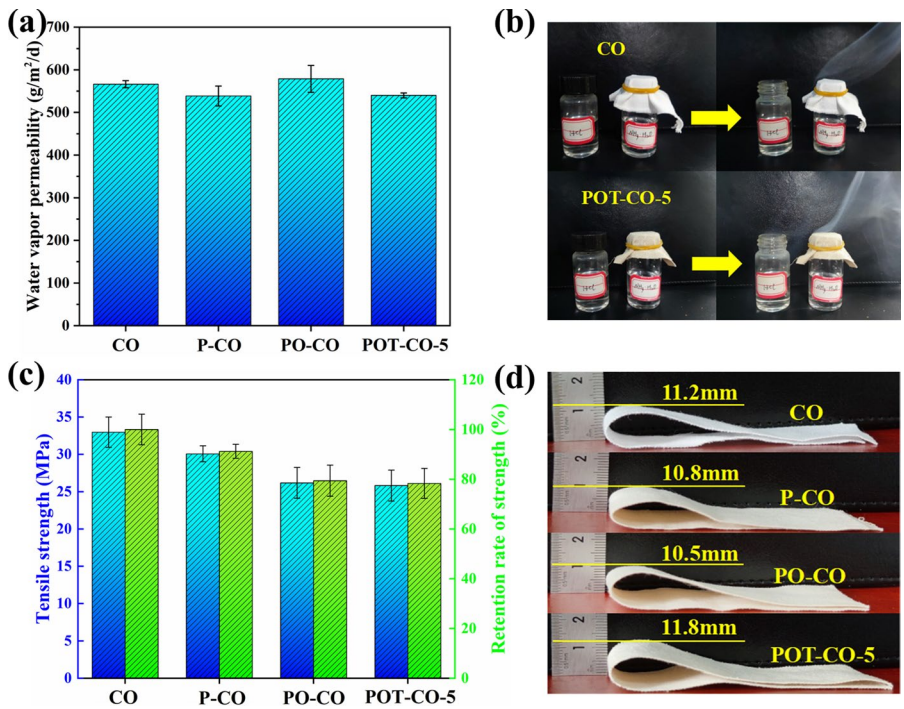


Fig. 12 Water vapor permeability (**a**), optical photos of water vapor permeability test (**b**), tensile strength (**c**), and flexibility (**d**) of the control cotton fabric and the modified fabrics

process. Specifically, cotton fabrics were successfully modified with bio-based materials PA, TiO_2 (NPs) and ODA in three steps. Firstly, PA molecules were covalently bonded to the cotton fiber surface through an esterification reaction to obtain the flame-retardant cotton fabric P-CO. Then, TiO_2 (NPs) and ODA were loaded onto the surface of P-CO fabric by atomization technique. ODA was not only grafted onto the surface of P-CO fabric by amide reaction, but also formed a thin film to fix the titanium dioxide particles on the surface of P-CO fabric. The resulted multifunctional cotton fabric (POT-CO-5) possessed excellent flame retardance (LOI = 48.5%), hydrophobic properties (contact angle = 52°), UV resistance (UPF = 2000) and antibacterial properties (BR = 100%) compared to the untreated cotton fabric. POT-CO-5 fabric also showed excellent resistance to washing, maintaining excellent flame retardance (LOI > 36.2%), hydrophobicity (contact angle > 138°), UV resistance (UPF = 2000) and antimicrobial properties (BR > 96.0%) even after 20 washing cycles. It was worth mentioning that the surface modification process provided cotton fabric versatility without significantly sacrificing desired cotton properties such as water vapor permeability, tensile strength and softness. Due to the combination of excellent multifunctionality and durability, POT-CO-5 fabric have a strong potential for the future application in the field of multifunctional textiles.

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Data availability Data available on request from the authors.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethics approval and informed consent The authors have no statement about ethical approval and informed consent. Because, this research does not involve human and animal.

Consent for publication All authors had read and agreed to the published version of the manuscript.

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