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# Preparation of functionalized cotton based on laccase-catalyzed synthesis of polyaniline in perfluorooctanesulfonate acid potassium salt (PFOS) template

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Enzymatic polymerization of aniline was first performed in a perfluorooctanesulfonate acid potassium salt,  $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{K}$ , abbreviated to PFOS, template system with *Aspergillus* laccase/ $\text{O}_2$  as catalyst and oxidant and then functionalized cotton, possessing special electro-optical properties and variable wettability, was prepared by *in situ* polymerization of aniline under optimal conditions. The chemical structure and composition characterizations of the cotton fabric were carried out using corresponding characterization techniques, which indicated that, in the process of *in situ* polymerization, the hydroxyl groups in cotton cellulose, to a certain extent, could also be involved in the reaction and confirmed that the hydrophobicity of treated cotton (with a maximal contact angle of approximately  $124^\circ$ ) was a result of the synergetic effect of low surface energy of PFOS and the coexistence of micro/nano structures on the cotton surface. The results of cyclic voltammetry, fiber resistance testing, and thermal analyses proved that the electro-optical properties and thermal stability of cotton fabric were drastically enhanced by PFOS-doped PANI. Utilizing the doping/dedoping process of PANI, the wettability of treated cotton underwent a reversible change from hydrophilic to hydrophobic. Color tests and zeta potential measurements served as auxiliary evidence to explain the mechanism of the wettability switch of the functionalized cotton. The stability of PFOS-doped PANI on the cotton surface was evaluated by a washing fastness test, which showed that the contact angle of the treated cotton could still reach  $94.5^\circ$  after 25 cycles of water washing.

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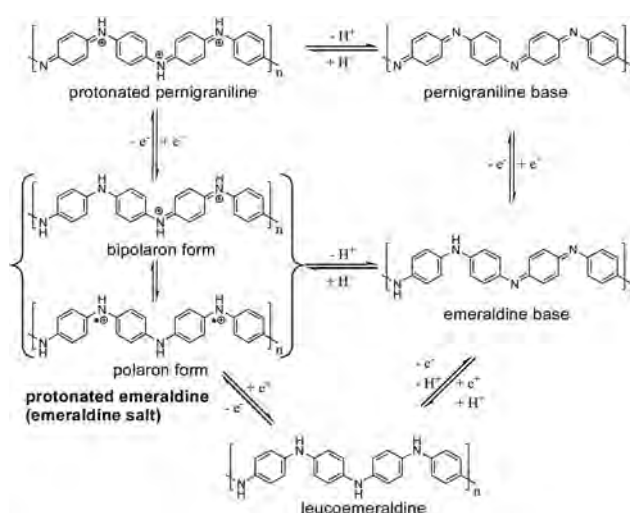
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## Introduction

Enzymatic polymerization of aniline has been investigated by various research groups, since the 1990s.<sup>1,2</sup> Laccase, a multi-copper oxidoreductase, can catalyze the oxidation of many substrates, with atmospheric oxygen as the oxidizing agent.<sup>3</sup> Compared to chemical and peroxidase-mediated oxidative polymerizations, laccase-catalyzed reactions are usually eco-friendly and can be carried out without the use of  $\text{H}_2\text{O}_2$ .<sup>4</sup> The pH-dependent transformation between a conducting salt (emeraldine salt, abbreviated to PANI-ES) and a nonconducting base (emeraldine base, abbreviated to PANI-B) illustrates that PANI can respond to the changes of external parameters by a change in the electro-optical and electro-chemical properties, a feature valuable in many fields of application.<sup>5,6</sup> The structural changes of polyaniline (PANI) based on different redox

conditions and protonated/deprotonated states are shown in Scheme 1. Since polymer chains of PANI are very long, detailed



Scheme 1 Structural changes of polyaniline based on different redox conditions and protonated/deprotonated states.

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structural analyses of PANI, such as by mass spectrometry and nuclear magnetic resonance (NMR) spectrometry, are very difficult.

Wettability of a solid surface is mainly governed by the chemical composition and the micro/nano structures on material surfaces.<sup>7,8</sup> Fabrics having low surface free energy, combined with the coexistence of micro/nano structures are generally hydrophobic and possess self-cleansing function properties, as dust and dirt from the fabric surfaces gets washed away with water. If natural fabrics having many hydroxyl groups and certain microstructures are used as substrates for polymers, nanostructures of polymers would be introduced onto the fabric surface and then the surfaces appearing like lotus leaves as well as the coexistence of micro/nano structures can be easily obtained. Simultaneously, introduction of functional polymers, such as PANI complex, will endow the fabrics with some special electro-optical properties, which allow the further exploration on the use of natural fabrics in the fields of electromagnetic shielding, color changing textiles, and gas detection.<sup>9–11</sup>

The aim of our research was to seek a simple method to prepare functionalized cotton. For the first time, the use of perfluorooctanesulfonic acid potassium salt (PFOS), a kind of fluorinated anionic surfactant usually used as an additive in defoaming agents,<sup>12</sup> as a template for laccase-catalyzed polymerization of aniline has been investigated. Structural characterizations of the treated cotton, using techniques such as AFM, FT-IR, and XPS, were carried out to demonstrate that the combination of low surface free energy of PFOS and coexistence of micro/nano structures on the functionalized cotton surface could result in good hydrophobicity of cotton fabric. Cyclic voltammetry, fiber resistance tests, color tests, and thermal analyses were carried out to demonstrate the improved electro-optical properties and thermal stability of cotton fabric. The surface charges (zeta potential) of the fibers were measured to clarify the mechanism of “wettability switch”<sup>13</sup> of functional cotton: the different attachment status of PFOS on PANI chains during PANI doping/dedoping process led to a reversible change in the wettability of treated cotton.

## Experimental section

### Materials

Laccase from *Aspergillus* sp. (EC1.10.3.2), having an enzyme activity of ca. 60 U g<sup>-1</sup>, was supplied by Novozymes (Shanghai, China). One unit of laccase was defined as the amount of enzyme required to oxidize 1 μmol of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) per minute at room temperature.<sup>14</sup> Prior to use, laccase powder was dissolved in deionized water to obtain a concentration of 200 mg mL<sup>-1</sup>. The stock solution was then obtained by centrifuging this mixture at 10 000 rpm for 10 minutes. PFOS and Nafion, exploited by DuPont Company, were purchased from Sigma-Aldrich. The cotton fabrics were desized prior to use. Aniline and all other reagents used were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). They were used without further purification. All solutions were prepared using deionized water.

### Laccase-catalyzed polymerization of aniline in PFOS template

A 65.0 mg PFOS sample was dissolved in 20 mL of 50 mM Na<sub>2</sub>HPO<sub>4</sub>-citric acid buffer (pH 4.5). Then 27.9–74.4 μL aniline was added to the above solution. Due to the poor solubility of PFOS and aniline in water, the solution was ultrasonically stirred to facilitate the homogeneous dispersion of the solutes. The pH of reaction mixture rose to about 4.9 due to the addition of PFOS and aniline, which was then brought back to 4.5. Briefly, the optimal reaction conditions for laccase-catalyzed polymerization of aniline in PFOS template system were as follows: 6 mM PFOS, 25 mM aniline, pH 4.5, 1.2 U mL<sup>-1</sup> laccase; the typical reaction conditions were 3 days at 5 °C. Due to the presence of PFOS, PANI was obtained in a doped form having green color and the suspension was quite stabilized in the first few hours (Fig. 1). However, the complexes separated out after 24 h and there were almost no complexes dispersed in water after 3 days (Fig. 1). The precipitate was collected by centrifugation and then thoroughly washed using deionized water. Finally the purified polymer was oven-dried at 60 °C for 24 h for further characterization.

### Preparation of functionalized cotton

A sample of cotton (about 4.0 cm<sup>2</sup>) was immersed into the reaction mixture before the addition of the laccase. Ultrasonically stirring was stopped when the solution was homogeneous and stable. The reaction was initiated by the addition of the laccase. Other reaction conditions are in accordance with the optical conditions mentioned above. The cotton sample was taken out after 3 days was repeatedly washed with deionized water before being dried in an oven at 60 °C. The same reaction without the inclusion of laccase was used as the reference.

### UV-Vis spectra analysis

UV-Vis spectra of PANI-ES-PFOS complexes were recorded on a UV-2808S UV-Vis spectrophotometer (Unicos, China), in the range of 200–1100 nm. The absorption bands at 430 and 775 nm

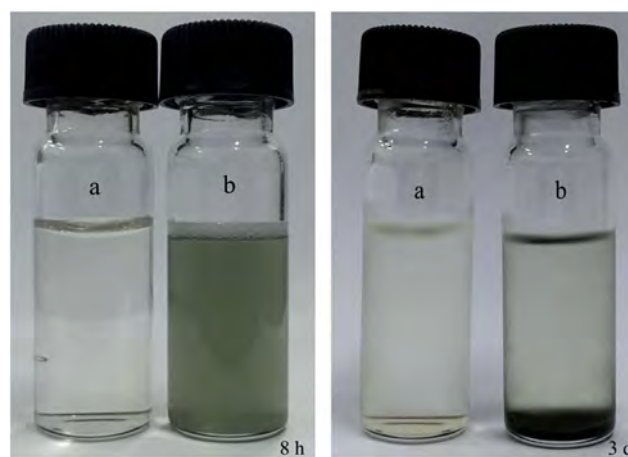


Fig. 1 Photographs of laccase-catalyzed polymerisation of aniline without (a) and with (b) PFOS template. [Aniline] = 25 mM, [PFOS] = 6 mM, 1.2 U mL<sup>-1</sup> laccase, different reaction time at pH 4.5 and 5 °C.

indicated the formation of polarons in PANI structure,<sup>15</sup> which make PANI and cotton conducting materials.

### SEM and EDX analyses

Scanning electron microscopy along with energy-dispersive X-ray spectroscopy of cotton samples were conducted using a S-3400N II scanning electron microscope (Hitachi, Japan), equipped with an EX-250 energy-dispersive X-ray spectrometer (Horiba, Japan).

### AFM analysis

The three-dimensional surface topography was analyzed using a CSPM 4000 atomic force microscope (Benyuan Co. Ltd.) with a scanning frequency of 2.0 Hz, referring to the work of Dong *et al.*<sup>16</sup>

### FT-IR spectroscopy

FT-IR spectra of the cotton samples and PFOS-doped PANI complex were recorded on a Nicolet iS10 infrared spectrophotometer (Thermo Nicolet, USA), using a conventional procedure. The spectra were recorded in the range of 4000–650  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  and 32 scans per sample.

### XPS characterizations

XPS analyses of cotton samples were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA) using aluminum as the source of radiation at 14 kV. Both the entire range spectra (0–1100 eV) and the narrow range spectra of all the elements were recorded using a RBD 147 interface (RBD Enterprises, USA) using an AugerScan 3.21 software.

### Cyclic voltammetry test

In order to verify the electroactive nature of functionalized cotton, cotton samples were tested with cyclic voltammetry using a CHI 660D electrochemical workstation (CH Instruments Inc., Austin, USA) at room temperature. Prior to the test, a small piece of functionalized cotton sample was glued to the glassy-carbon electrode by drying Nafion emulsion (1.5 wt%). The electrolyte was 50 mM  $\text{Na}_2\text{HPO}_4$ -citric acid buffered solution (pH 4.5).

### Measurement of fiber resistance

The resistance of cotton fibers was measured using a 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., USA) using two wires, drawn from a fixture box, tied to both the ends of cotton fibers at a certain distance.

### Color test

The color strength of cotton samples ( $K/S$ ) was evaluated at 580 nm using a 7000A reflectance measuring apparatus (Gretagmacbeth, USA).  $K/S$  was the Kubelka–Munk relationship and the  $K/S$  values were calculated from the Kubelka–Munk equation:

$$K/S = (1 - R)^2/2R \quad (1)$$

where,  $K$  was the absorbance coefficient,  $S$  was the scattering coefficient, and  $R$  was the reflectance.<sup>17</sup>

### Measurement of water contact angles (CA)

The wettabilities of the cotton samples were expressed as water contact angles, measured using a SL200B static contact angle/interfacial tension meter (Kino Industry Co. Ltd., USA). For each sample, the water contact angle was measured at three spots, and the average of the three readings was reported. The variable wettability of functionalized cotton was determined by measuring its contact angles after treatment with alkaline gases (pH 12.0), which included ammonia gas and ethylenediamine gas, or 6.0 mM PFOS solution (pH 3.0) for 2 min. The cotton was dried at 60 °C, prior to testing. All digital photographs were captured by an iPhone 6 (Apple Inc., USA).

### Zeta potential measurement

Surface zeta potential of the cotton fabric was measured using a SZP06 Zeta Potentiostat System (Mütek, Germany). The measurement was carried out using 500 mL reaction suspension, containing 4.0 g paper pulp, used as filling material, and 2.0 g comminuted cotton fibers. For each sample, the surface zeta potential was measured three times and the average of three reading was reported.

### Durability test

The stability of PFOS-doped PANI complex on the surface of cotton fabric after repeated standard washing was evaluated by the American Association of Textile Chemists and Colorists (AATCC) Test Method 61-1996. Cotton samples (approximately 4.0  $\text{cm}^2$ ) were introduced into stainless steel canisters, which contained 75 mL of aqueous solution containing 0.15% AATCC and 25 stainless steel balls. Due to the pH-dependence transition of PANI, the pH of aqueous detergent solution was adjusted to 4.5. The stainless steel canisters were then fixed in a Launder-Ometer® (Darong Textile Instrument Co., Ltd., China) and spun at 42 rpm for 45 min at 49 °C. In this method, each cycle of washing is equivalent to five washing machine cycles.<sup>18</sup> After the equivalent of 5, 10, or 25 washing cycles, the cotton samples were rinsed with deionized water and dried at 60 °C.

### Thermal analysis

The thermogravimetric analysis (TGA) of cotton samples was conducted on a TGA/SDTA851 thermal analysis system (Mettler Toledo, Switzerland) in the temperature range of 35–800 °C at a heating rate of 20 °C  $\text{min}^{-1}$ .

## Results and discussion

### General observations and experimental conditions

Serving as a dopant and a soft template, PFOS facilitated the head-to-tail coupling of the monomers by laccase. This was



essential for the laccase-catalyzed synthesis of doped PANI, just like any other soft templates that were reported previously for the enzymatic syntheses of conducting PANI.<sup>9–11,15,19</sup> Since aniline was excess compared to PFOS and there were not enough templates in the reaction system to provide plenty negative charges, particles of PANI-ES-PFOS precipitated due to the lack of charges when the complex grew larger in size (Fig. 1).<sup>20</sup> In addition, a low surface free energy of PFOS could also contribute to the complex precipitation. Briefly, it was quite easy to obtain the functionalized cotton since the complex deposited instantaneously on the cotton surface after the reaction.

In the enzymatic synthesis of conducting PANI complex, pH always played an important role, due to the  $pK_a$  of aniline and the enzymatic nature of the reaction.<sup>9–11,15,19</sup> Anilinium cations undergo oxidation reaction under acidic conditions by a reaction route different than taken by neutral aniline molecules, which are predominant in alkaline conditions.<sup>21,22</sup> In this paper, the optimal pH for laccase-catalyzed aniline polymerization with PFOS template was found to be 4.5 (Fig. 2a), which was the same as our previous work, in which laccase-catalyzed polymerization of aniline was carried out using sodium dodecylbenzenesulfonate (SDBS) template.<sup>9</sup>

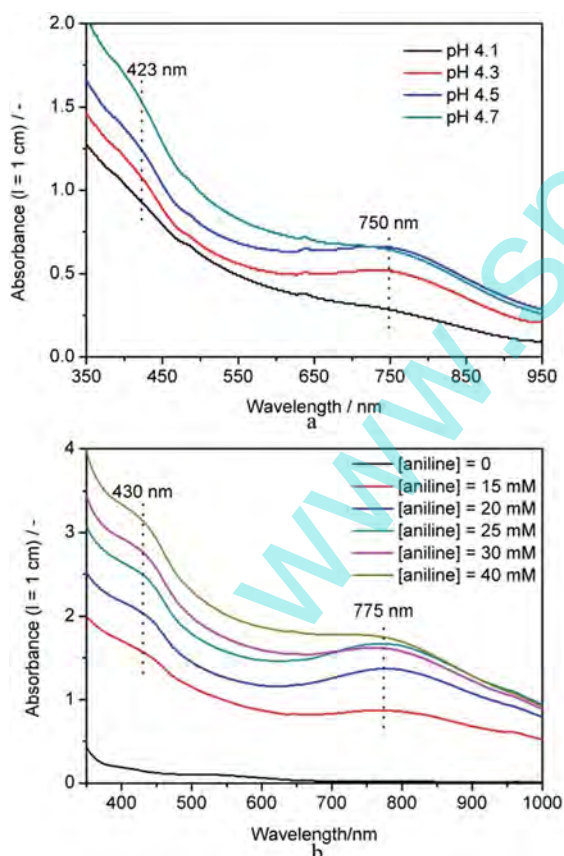


Fig. 2 Effect of pH (a) and aniline concentration (b) on the polymerization with PFOS template. Conditions a: [PFOS] = 6 mM, [aniline] = 25 mM, 1.2 U mL<sup>-1</sup> laccase, 8 h at 5 °C. Conditions b: [PFOS] = 6 mM, 1.2 U mL<sup>-1</sup> laccase, 24 h at pH 4.5 and 5 °C. The samples were shaken before the spectrum was recorded due to product precipitation.

Besides pH, molar ratio of aniline to PFOS was also crucial for the laccase-catalyzed synthesis of conducting PANI. UV-Vis spectra of laccase-catalyzed aniline polymerizations using 6.0 mM PFOS and different aniline concentrations are shown in Fig. 2b. The UV-Vis spectra of the PFOS-doped PANI complex had a peak at 775 nm when aniline/PFOS molar ratio ranged between 3.3 : 1 and 4.2 : 1. The cotton obtained under these conditions was also electroactive with green color, which will be discussed later in Fig. 5.

### Characterization of the structure of functionalized cotton

SEM (Fig. 3a and d) and AFM images (Fig. 3b and e) of the control cotton sample and functionalized cotton sample showed that after laccase-catalyzed *in situ* polymerization of aniline, the surface morphology of cotton became irregular and rough. The values of roughness of the control cotton and functionalized cotton, obtained from AFM data, were found to be approximately 64.7 nm and 106.0 nm, respectively. The granules appearing on the surfaces of the functionalized cotton were considered to be PFOS-doped PANI, which was confirmed by the EDS spectra (Fig. 3c and f) of cotton samples. The X-ray elemental maps of fluorine revealed that, after *in situ* polymerization, the hydrophobic PFOS-doped PANI particles were distributed homogeneously over the entire cotton surface. No fluorine signal was detected in case of the reference cotton sample. As there are many hydroxyl groups on the cotton surface, the adsorption of PFOS-doped PANI might be resulted from hydrogen bonds between PANI chains and hydroxyl groups on the cotton sample. The protonation of imine nitrogens of PANI, due to interactions with the hydroxyl groups of cotton, could have also improved the connectivity between the complex and cotton sample.<sup>9,23</sup> As could be seen from Fig. 3a and d, the magnitude of the diameter of a single cotton fiber bundle was in the order of microns and the diameter of the enclosed PANI particles was approximately several microns to a few hundred nanometers. It could be speculated that the micro structures of cotton and nanostructures of PFOS-doped PANI particles made up the rough surface of cotton, similar to that of the lotus leaves, which made it conducive to intercept air and enhance the hydrophobicity of materials.

FT-IR spectra of PFOS-doped PANI, functionalized cotton, and a reference cotton sample are shown in Fig. 4a. The peak at about 3500 cm<sup>-1</sup> was attributed to the N-H vibrations in PANI. The peaks at 1581 and 1495 cm<sup>-1</sup> were attributed to the C=C stretching of the quinoid and benzenoid rings of PANI.<sup>24</sup> The peaks between 1100 cm<sup>-1</sup> and 1300 cm<sup>-1</sup> were rather complex due to the overlap of C-N stretching and S=O stretching modes of sulfonic acid.<sup>25</sup> The peak at 1080 cm<sup>-1</sup> was due to the C-F vibrations of PFOS. The head-to-tail coupling of monomers, which led to the formation of linear polymeric chains, was ascertained by the peak at 808 cm<sup>-1</sup>.<sup>26</sup> These peaks confirmed the presence of PFOS-doped PANI on the surface of functionalized cotton. Peaks corresponding to neither PANI nor PFOS appeared in the spectrum of the reference cotton sample.

It should be noted that the FT-IR spectrum of the functionalized cotton was not a simple superimposition of that of control cotton and PFOS-doped PANI complex. Compared to the

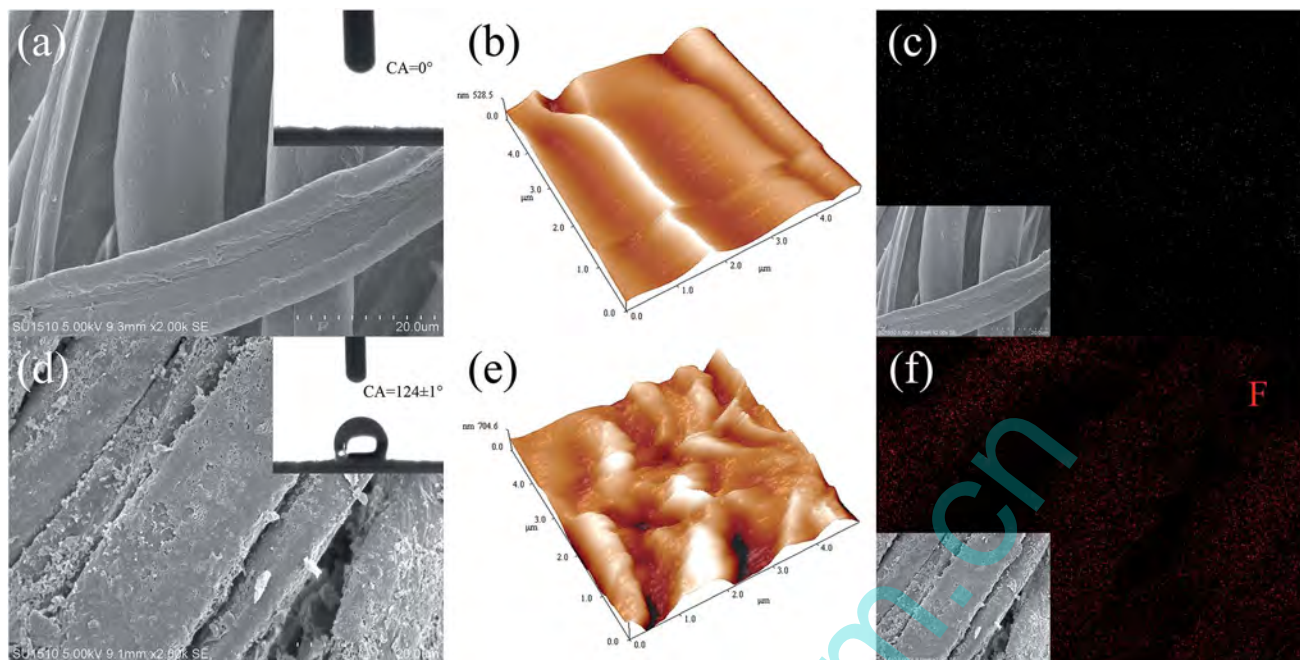


Fig. 3 SEM, AFM images and X-ray maps of fluorine of control cotton sample (a–c) and functionalized cotton sample (d–f). Insets are images of water droplet on the cotton surface (a and d) and corresponding SEM images of EDS (c and f).

superimposition, the intensities of the peaks at about  $3300\text{ cm}^{-1}$  weakened distinctly and some new peaks appeared between  $900$  and  $1000\text{ cm}^{-1}$  in the spectrum of the functionalized cotton. This indicated that in addition to the polymerization of aniline monomers, the hydroxyl groups on cotton fibers were also probably involved in the process of *in situ* polymerization. The reduction in the intensities of the peaks at about  $3300\text{ cm}^{-1}$  could also have been a result of the complex coating that led to the hydroxyl groups on cotton surface getting covered. The types of interactions of the hydroxyl groups on cotton fibers, which could be hydrogen bonding or protonation, which have also been mentioned in the SEM and AFM discussions, could be confirmed by XPS. As shown in O 1s core level spectra (Fig. 4b), the binding energy of O 1s of functionalized cotton decreased significantly (from  $532.1\text{ eV}$  to  $531.2\text{ eV}$ ) compared to that of the reference cotton sample, which indicated that the electron density on oxygen increased due to the participation of hydroxyl groups of cotton in the reaction.

Table 1 Composition of surface composition of control cotton and functionalized cotton resulting from XPS

Samples	Relative surface composition (%)					C/N ratio
	C	O	N	S	F	
Control cotton	62.26	36.96	0.49	0.18	0.00	148.24
Functionalized cotton	41.06	23.53	4.97	5.59	31.57	9.64

The relative surface composition (Table 1) of control cotton and functionalized cotton, obtained from the results of quantitative XPS analysis was in accordance with XPS wide scan (Fig. 4c). Relatively large amounts of nitrogen, fluorine, and sulfur elements were detected on the functionalized cotton surface and the ratio of total carbon to nitrogen on electroactive cotton surface was also much lowered than that of the control cotton. All these data confirmed the presence of PFOS-doped PANI complex on the surface of functionalized cotton.

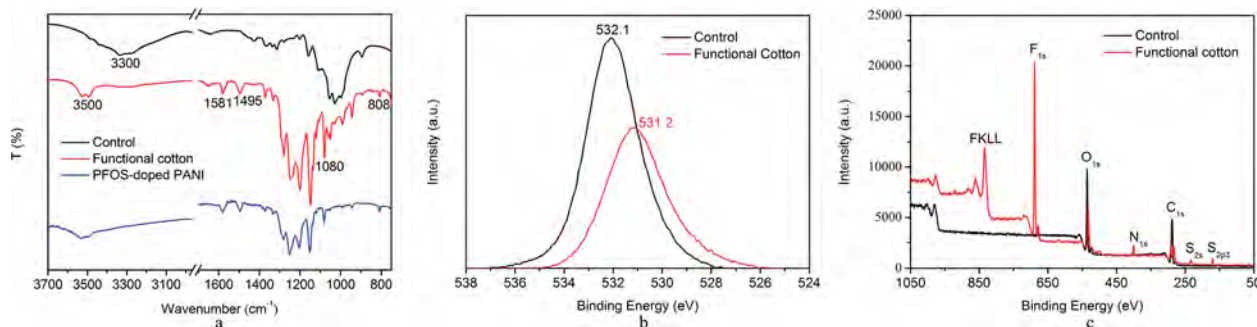


Fig. 4 FT-IR spectra (a), O 1s core level spectra (b) and XPS wide scan (c) of control cotton sample, functionalized cotton.

### Electroactivity of functionalized cotton

The functionalized cotton obtained with an aniline/PFOS molar ratio of 4.0 : 1 was electrochemically active in 50 mM Na<sub>2</sub>HPO<sub>4</sub>-citric acid buffered solution (pH 4.5). As shown in Fig. 5, two pairs of reversible symmetrical redox peaks appeared in the cyclic voltammogram of functionalized cotton, which confirmed its electrochemical activity and illustrated its potential application in flexible electronic devices.

In the field of synthesis of conducting PANI, low pH value is conducive for doping and conductivity of the polymer. Therefore, the conductivity of PANI produced by enzymatic catalysis methods tends to be two orders of magnitude lower than that of PANI obtained from traditional chemical methods, which are performed in strongly acidic media. The conductivity of PFOS-doped PANI produced by enzymatic catalysis is about  $1.0 \times 10^{-4}$  S cm<sup>-1</sup>. However, the conductivity of the coated fiber was more than the range of four-probe electrical conductivity instrument. The resistance of cotton samples was ultimately measured using a semiconductor parameter analyzer and the results were given in Fig. 6. The fiber resistances in Fig. 6b were obtained from the slopes in Fig. 6a with three replicates. As can be seen from Fig. 6a or b, the resistance of a single cotton fiber (sample B) coated with the PFOS-doped PANI complex decreased by a magnitude of approximately five orders compared with the control cotton fiber (sample A), which suggested a conceivable prospect for use of natural fibers in electronic devices. The other two samples indicated that short fibers (sample C) or multiple fibers connected in parallel (sample D) had relatively low resistance. These phenomena were consistent with the electrical rule, according to which, shortening the length of resistors and connecting the resistors in parallel would reduce the resistance of resistors.

### Variable wettability of functionalized cotton

Wettability is one of the most important characteristic features of a solid surface and transition of wettability of materials between hydrophobic and hydrophilic, by adjusting the roughness and chemical structures on material surfaces, has

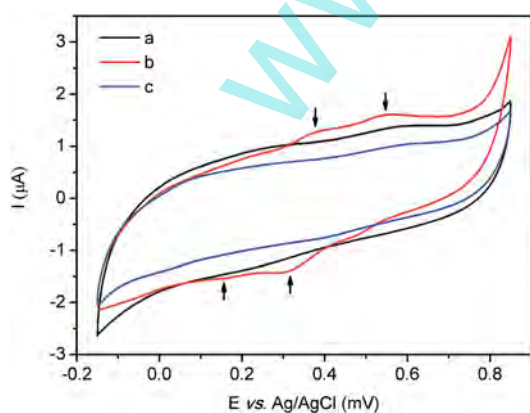


Fig. 5 Cyclic voltammograms of control cotton sample (a) and functionalized cotton prepared at an aniline/PFOS of 4.0 : 1 (b) and 7.0 : 1 (c) recorded at pH 4.5.

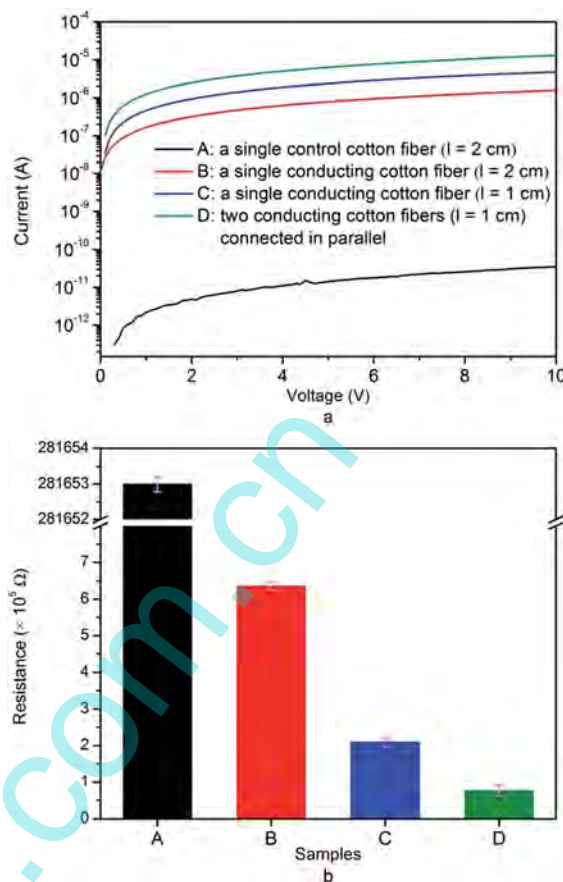


Fig. 6 The current vs. voltage of treated cotton fiber under different test conditions (a) and fiber resistance obtained from three replicates (b).

great scientific significance,<sup>27–31</sup> especially in the fields involving microfluidic devices, self-cleaning surfaces, biomedical engineering, *etc.*<sup>32–35</sup> At present, a large number of innovative methods have been employed for the activation of wettability switches, such as electric activation,<sup>13,36</sup> temperature activation,<sup>37</sup> and light activation.<sup>38,39</sup> Different from PANI-ES-SDBS functionalized cotton in our previous work,<sup>9</sup> PANI-ES-PFOS functionalized cotton possessed not only electro-optical properties but also variable wettability. In this study, the functionalized cotton obtained primordially was hydrophobic (Fig. 7a), due to the synergetic effect of the low surface energy of PFOS and the coexistence of micro/nano structures on the cotton surface. Nevertheless, the functionalized cotton was rendered hydrophilic after treatment with ammonia gas and ethylenediamine gas for 2 min (Fig. 7b). This change in wettability was reversible as the functionalized cotton could be rendered hydrophobic again on treatment with 6.0 mM PFOS solution (pH 3.0) for another 2 min. When ethylenediamine and ammonia had the same concentrations, the pH value of ethylenediamine is higher than ammonia due to the strong alkaline nature of ethylenediamine and the dedoping speed of ethylenediamine gas was also faster than ammonia gas, confirmed by the speed of color change of cotton samples. However, either ethylenediamine or ammonia could dedope the functionalized



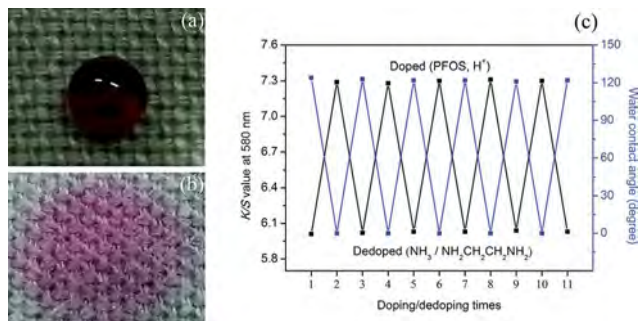


Fig. 7 Photos of hydrophobic cotton (a) and hydrophilic cotton (b) and reversible hydrophobic–hydrophilic conversion of the treated cotton through doping with PFOS and dedoping with ammonia or ethylenediamine gas (c). 2 doping/dedoping times refer to a doping/dedoping cycle, the same with Fig. 9. The water drops were colored with red dyes.

cotton completely at pH 12.0 for 2 min and the contact angle of the cotton fabric reached a maximum when the fabric was completely dedoped. The repeated reversibility of color and wettability properties of functionalized cotton, by doping with PFOS and dedoping with ammonia or ethylenediamine gas, is shown in Fig. 7c. The contact angle of functionalized cotton prepared at pH 4.9 with an [aniline]/[PFOS] ratio of 4 : 1 was found to be as high as  $124^\circ$  (Fig. 3d).

The mechanism of wettability switch of functionalized cotton is proposed in Fig. 8. After treatment with alkaline gas, the color of cotton transformed from green to blue-purple and the cotton was no longer able to conduct, as a result of the dedoping of PANI. Meanwhile, the dopants, PFOSs, were no longer fixed to PANI chains, but were free to move. When water drops fell on the surface of cotton, the hydrophilic groups of PFOS,  $\text{SO}_3^-$ , arranged themselves in the direction pointing towards water, thereby turning the wettability of functionalized cotton towards hydrophilic. After treatment with PFOS acid solution, PANI was in the doped form and the cotton appeared green in color and started conducting again. Simultaneously, the hydrophilic groups of PFOS were bound to the PANI chains and the hydrophobic groups of PFOS were arranged pointing

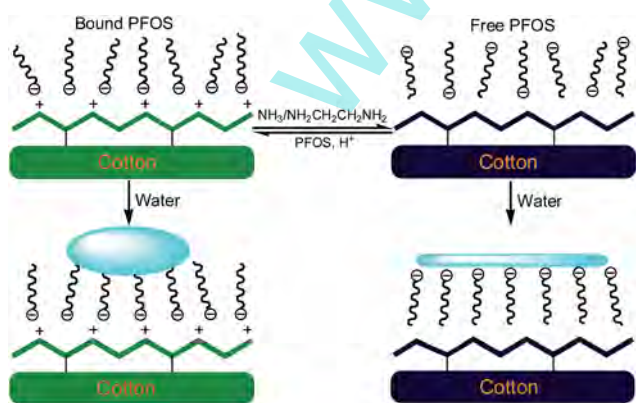


Fig. 8 Schematic illustration of wettability switch of functionalized cotton based on laccase-catalyzed synthesis of polyaniline in PFOS templates.

outwards, making the functionalized cotton hydrophobic again. This reversible change of wettability of functionalized cotton was termed “wettability switch”.

The mechanism of wettability switch of functionalized cotton could also be further confirmed by the determination of the zeta potentials. Fig. 9 shows that the zeta potential of the suspension of the reference cotton sample, which had paper pulp as the filling material was  $-28.3$  mV, paper pulp accounting for the most of it. After *in situ* polymerization of aniline, the hydroxyl groups on the surface of the cotton fabric were covered with PFOS-doped PANI complex particles. The zeta potential of the suspension of hydrophobic cotton sample and filling materials was thus lower ( $-25.5$  mV) than that of the reference cotton sample and filling materials. After treatment of the cotton with alkaline gas, the exposed sulfonic groups in PFOS endowed the cotton fabric with a high zeta potential ( $-36.6$  mV). The zeta potential of filling materials and cotton with 3 cycles of doping/dedoping again went back to approximately  $-25.5$  mV, which suggested the starting of a new doping/dedoping cycle. In short, the reversible changes in zeta potentials of the slurries corresponded to the conversion of electro-optical properties and wettability of the functionalized cotton through a doping/dedoping process.

## Washing fastness

The stability of PFOS-doped PANI on the cotton surface was evaluated using the AATCC standard washing test method (AATCC 61-1996) and the results are presented in Fig. 10. The contact angle between functionalized cotton and water droplets decreased during the first 15 cycles of water washing. Although the reaction of hydroxyl groups in cotton fabrics during the *in situ* polymerization of aniline was discussed based on FT-IR and XPS analysis, the forces between the cotton fabric and PFOS-doped PANI are not totally clear at this moment. The fastness of PFOS-doped PANI on the cotton surface might not be ideal, but the contact angle could still reach  $94.5^\circ$  after 25 cycles of water washing, which suggested of a hydrophobic character of the functionalized cotton fabric after repeated water washing.

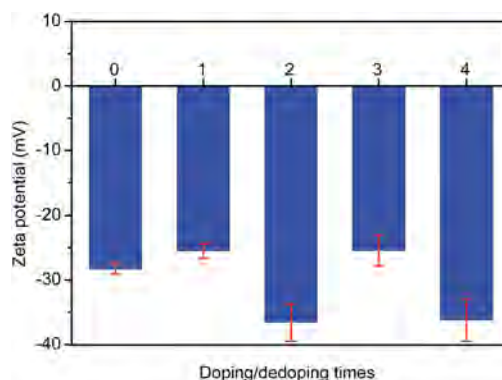


Fig. 9 Zeta potential of the slurry of paper pulps and cotton sample with different doping/dedoping times. The sample with doping/dedoping time of 0 refers to paper pulps and the reference cotton fabric.

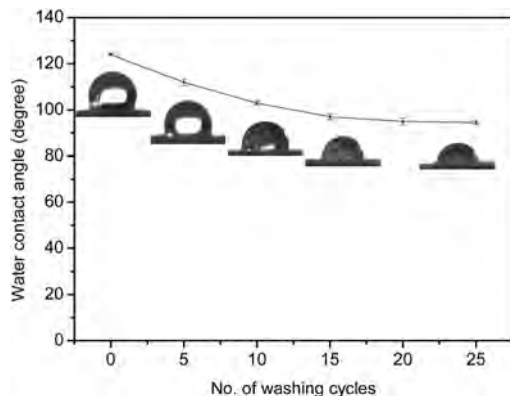


Fig. 10 The water contact angles vs. washing cycles of functionalized cotton. Insets are images of water droplet on the treated cotton surfaces.

### Thermal analysis of functionalized cotton

The pyrolytic characteristics of the control and functionalized cotton are shown in Fig. 11. These fabrics started to decompose at the same temperature (300 °C). However, the main weight loss of functionalized cotton ended at 419 °C, representing an increase of 11 °C compared to that of the control cotton (408 °C). The difference in thermal stability between control cotton and functionalized cotton became noticeable at 408 °C, which showed 12.3% and 29.2% solid residues for control cotton and functionalized cotton, respectively. The control cotton showed the maximum rate of mass loss (3.40 wt%/°C) at 400 °C, when most of the cotton was pyrolyzed, with 0.6% solid residue remaining at 800 °C. In contrast to this, the functionalized cotton attained its maximum rate of mass loss (1.92 wt%/°C) at 406 °C, and still showed a solid residue of 11.1% even at 800 °C. It could also be seen from Fig. 11 that the degradation of cotton mainly occurred between 300 and 408 °C, while the degradation of PFOS-doped PANI mainly occurred between 419 and 530 °C with a maximum mass loss of 0.30 wt%/°C at 497 °C. Based on the above discussions, it could be concluded that PFOS-doped PANI had better heat

resistance than cotton and that the thermal properties of cotton were enhanced by *in situ* polymerization of aniline.

## Conclusions

In this study, functionalized cotton with special electro-optical properties and variable wettability was obtained by laccase-catalyzed *in situ* polymerization of aniline in PFOS template. FT-IR and XPS analyses suggest the formation of some chemical bonds between PFOS-doped PANI and cotton fibers, in the process of *in situ* polymerization of aniline by laccase. Therefore, the obtained functionalized cotton remained hydrophobic even after 25 cycles of water washing (with a contact angle of 94.5°). The hydrophobicity of the functionalized cotton could probably be the result of the coexistence of micro/nano structures on the functionalized cotton surface which also have low surface free energies, owing to the introduction of PFOS. Based on cyclic voltammetry tests and measurement of fiber resistance, the cotton obtained was electroactive at pH 4.5 with an aniline/PFOS molar ratio ranging from 3.3 : 1 to 4.2 : 1. Color tests and electrical tests proved the electro-optical properties of functionalized cotton. In this paper, PFOS was not only used first as a template and a dopant in laccase-catalyzed synthesis of conducting polyaniline (PANI), but it also endowed the cotton fabric with a characteristic variable wettability. The measurement of charges on the fiber surface confirmed that the different attachment status of PFOS during PANI doping/dedoping process led to the reversible change of wettability of functionalized cotton. The thermal analyses demonstrated an improved thermal stability of treated cotton.

As PFOS is unfriendly to the environment, other soft templates which are nontoxic or low-toxic could be found as alternative templates for the polymerization of aniline in the future. The functionalized cotton obtained with that alternative template may have some promising applications in the field of military and sensing technology. Briefly, the research presents a promising approach for preparing functional textiles.

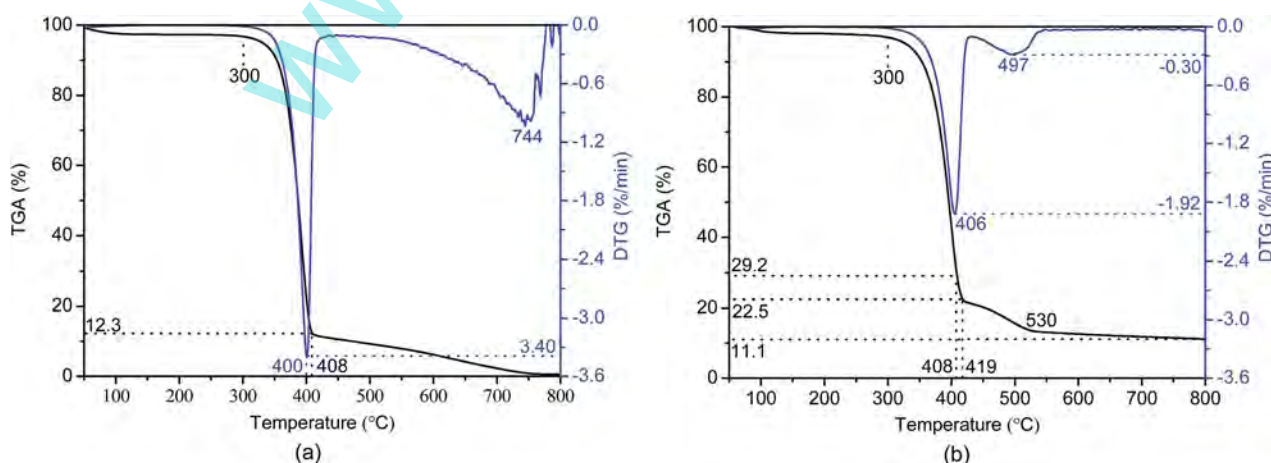


Fig. 11 TGA and DTG curves for control cotton (a) and the functionalized cotton (b).



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