## PAPER

# Smart color-changing textile with high contrast based on a single-sided conductive fabric†

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An electrically triggered color-changing fabric was prepared *via* a facile and low-cost approach combining the resistive heating properties of a conductive fabric and the color-changing properties of thermochromic materials. The conductive substrate was produced by the selective deposition of PPy on the cotton side of a commercially available polyester-covered cotton fabric, while the thermochromic ink was painted on the polyester side. The smart fabric showed remarkable resistive heating and color-changing properties under an applied current with bright color contrast due to the light color of the conductive substrate.

## Introduction

Although smart watches and intelligent bracelets have been recognized by the market and customers, they are not the end of wearable devices. As the development direction of new wearable devices in the future, smart fabrics and electronic textiles are being increasingly investigated.[1–3] These textiles will go beyond their traditional roles of protection and fashion and consequentially offer people more intelligent services. Among them, smart color-changing fabrics or fibers have become a hotspot for their various potential applications, such as non-emitting displays, sensors, military camouflage and ornaments.[4–8] Currently, some commercially available fabrics can also change their colors upon encountering diverse stimuli like temperature or ultraviolet radiation. However, this color change is passive because it is uncontrollable for users. In comparison, using electricity as a trigger to drive the color change is a more easily and efficiently controllable approach. It is well known that when the electroactive species undergo electrochemical oxidation or reduction reactions, their optical absorption bands can reversibly change, caused by the gain or loss of electrons.[9] Therefore, electrochromism makes the active control of color change possible. Traditional electrochromic devices have found important applications in the fields of e-paper, antiglare rear-view mirrors in cars,

energy-saving smart windows, *etc.*[10,11] But actually the age of electrochromic fabric has not yet come. The fabrication of flexible electrochromic fabrics is difficult since it requires real flexible transparent electrodes to display the color changes and the encapsulation of devices to avoid electrolyte leaks.[9,12] While a few electrochromic fabrics or fibers have been reported to date,[13–18] there is still a long way to go before the emergence of applicable electrochromic fabrics.

Considering that flexible electrochromic fabrics are difficult to realize, some scientists as well as artists have used a simpler approach to design and manufacture electrically driven color-changing fabrics which combines the resistive heating properties of a conductive substrate and the color-changing properties of thermochromic materials.[1,19–22] The most common approach is to weave or sew metallic yarns within fabrics and then paint thermochromic inks on top of them.[19] This strategy has its own drawbacks since the color change can only happen in the place close to the conductive yarn when a current is passed through. In a recent article, Laforgue *et al.* used poly-3,4-ethylene-dioxythiophene (PEDOT), a widely used conductive polymer, to produce a non-woven mat.[20] The mat is wholly conductive so that a pattern drawn with a thermochromic ink can undergo a color change when the power is switched on. Nevertheless, this mat may inherit the inherent disadvantages of non-woven fabrics and the dark blue background color should have a certain influence on the effect of the color change. Later, they prepared a coaxial multilayer monofilament whose conductive core layer could trigger the color change of the external thermochromic layer upon resistive heating.[22] However, the conductivity of the monofilament is low, so a relatively high voltage was needed to induce the color change, and it may be challenging for some applications such as wearable fabrics where high voltages are not allowed. Besides, it seemed that the color

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change of the manually woven fabric from monofilaments was not obvious enough.

Herein, we have developed a simple and low-cost approach to obtain a smart color-changing fabric with high contrast by designing a two-layered integrated structure. A commercially available polyester-covered cotton fabric was used as a substrate directly, which saved weaving steps from monofilaments and ensured the wearability of the smart fabric. Conducting polymers of polypyrrole (PPy) with high stability and electrical conductivity were selectively grown on the surface of the cotton layer to provide resistive heating for the color change. Thermochromic materials were screen printed on the polyester face for the color appearance. Due to the double-faced structure of the fabric, the dark conductive PPy on the cotton face did not interfere with the color of the thermochromic materials on the light-colored polyester face, thus ensuring effective color changes. This new smart fabric exhibits good color-changing properties under the control of electricity. Moreover, it is completely wearable by virtue of the substrate.

## Experimental section

### Reagents and materials

Pyrrole, sodium dodecyl sulfate (SDS), ammonium persulfate (APS), $FeCl_3 \cdot 6H_2O$, and sodium anthraquinone-2-sulfonate (NaAQS) were obtained from Sinopharm Chemical Reagent Co., Ltd. Pyrrole was freshly distilled, while all other chemicals were used as supplied. All aqueous solutions were prepared with Milli-Q water ($\sim$18 M$\Omega$). The polyester-covered cotton fabric was a commercially available knitted fabric with double-faced structure purchased from Zhejiang China Light & Textile Industrial City Group Co., Ltd. Before the deposition of PPy, the fabric was immersed in an aqueous solution of sodium hydroxide (1 M) for 1 h to remove grease and other impurities attached on it, followed by soaking and rinsing with $H_2O$ until neutral pH was reached. Thermochromic inks (1935C, 350C and 301C; color-changing type: decoloration) with a color transition temperature of 45 $^{\circ}$C were purchased from Shenzhen Qianbian Pigment Co., Ltd. The viscosity of the thermochromic inks is 40 000 CPS and the tinting strength is 90%.

### Preparation of black conductive fabric

A fabric sample (6 × 6 cm) was immersed in 50 mL aqueous solution of pyrrole monomer (0.69 mL, 0.01 mol) and kept at 0 $^{\circ}$C for 20 min, followed by the addition of a 50 mL aqueous solution of $FeCl_3 \cdot 6H_2O$ (2.7 g, 0.01 mol) and sodium anthraquinone-2-sulfonate (0.39 g, 1.25 mmol) dropwise to initiate polymerization. The polymerization reaction was performed at 0 $^{\circ}$C for 1 h. The coated fabrics were then washed with water and dried at ambient temperature. The average surface resistivity was 30 $\Omega$ sq$^{-1}$.

### Preparation of single-sided conductive fabric

A fabric sample (6 × 6 cm) was immersed in a 50 mL aqueous solution of pyrrole monomer (0.69 mL, 0.01 mol) and SDS (0.58 g, 2 mmol) and kept at 0 $^{\circ}$C for 20 min, followed by the addition of 50 mL of an aqueous solution of APS (1.14 g, 5 mmol) dropwise to initiate polymerization. The polymerization reaction was performed at 0 $^{\circ}$C for 1 h. The coated fabrics were then washed with water and dried at ambient temperature.

### Preparation of color-changing fabric

The color-changing fabric was prepared by manual screen printing. A conductive fabric substrate was put under the image of the screen. The thermochromic ink was diluted with the same weight of pure water in order to decrease its viscosity and then placed on the screen surface. A squeegee was attached to the screen and drawn linearly along the screen to force the thermochromic ink through the screen onto the fabric substrate. Finally, the painted fabric was dried at ambient temperature.

### Characterization

The surface morphologies of the fabrics were characterized by scanning electron microscopy (SEM, Hitachi FE-SEM S-4800 operated at 1 kV). The surface resistance was determined according to the American Association of Textile Chemists and Colorists Test Method 76-1995. Two rectangular steel electrodes were placed on the fabric sample and the surface resistance ($R_s$) was given by $R_s$ ($\Omega$ sq$^{-1}$) = $WR'/D$, where $R'$ is the resistance measured by the multimeter, and $W$ and $D$ are the width of the sample and the distance between the two steel electrodes, respectively. The temperature distributions of the fabric under an applied current were recorded on a professional infrared thermal imaging camera (FLIR Therma CAM A300). The temperature of a circular region with a diameter of 5 mm located at the center of the sample was recorded using a portable infrared thermometer (Fluke 62 Mini). The photographs and videos were taken using a digital camera (Nikon, D7100). Stretching tests were conducted using a Hengyi Table-Top universal testing instrument. The substrate size was 35 mm × 35 mm. The fabric was elongated/released at a speed of 3.3% s$^{-1}$. The concomitant resistance was measured using a Victor VC9807A$^+$ digital multimeter during the stretching cycle. Abrasion resistance measurement was carried out using a rubbing fastness tester (Y571B, Changzhou Alpha Machinery Manufacturing Co., Ltd, China). A specimen of the single-sided conductive fabric (2.3 cm × 2.1 cm) was mounted on the bottom holder of the tester, and subjected to abrasion cycles. Air permeability of the samples was measured using an air permeability tester (YG461E, Ningbo Textile Instrument Factory, China).

## Results and discussion

A commercially available polyester-covered cotton fabric was used as the substrate (Fig. 1a). It has a double-faced structure with one side woven from cotton fibers and the other side from polyester fibers (Fig. 1b–h). As a result, this fabric has the merits of both cotton and polyester fabrics, including breathability and durability, which renders its broad application in the consumer clothing industry. Because of the relatively high
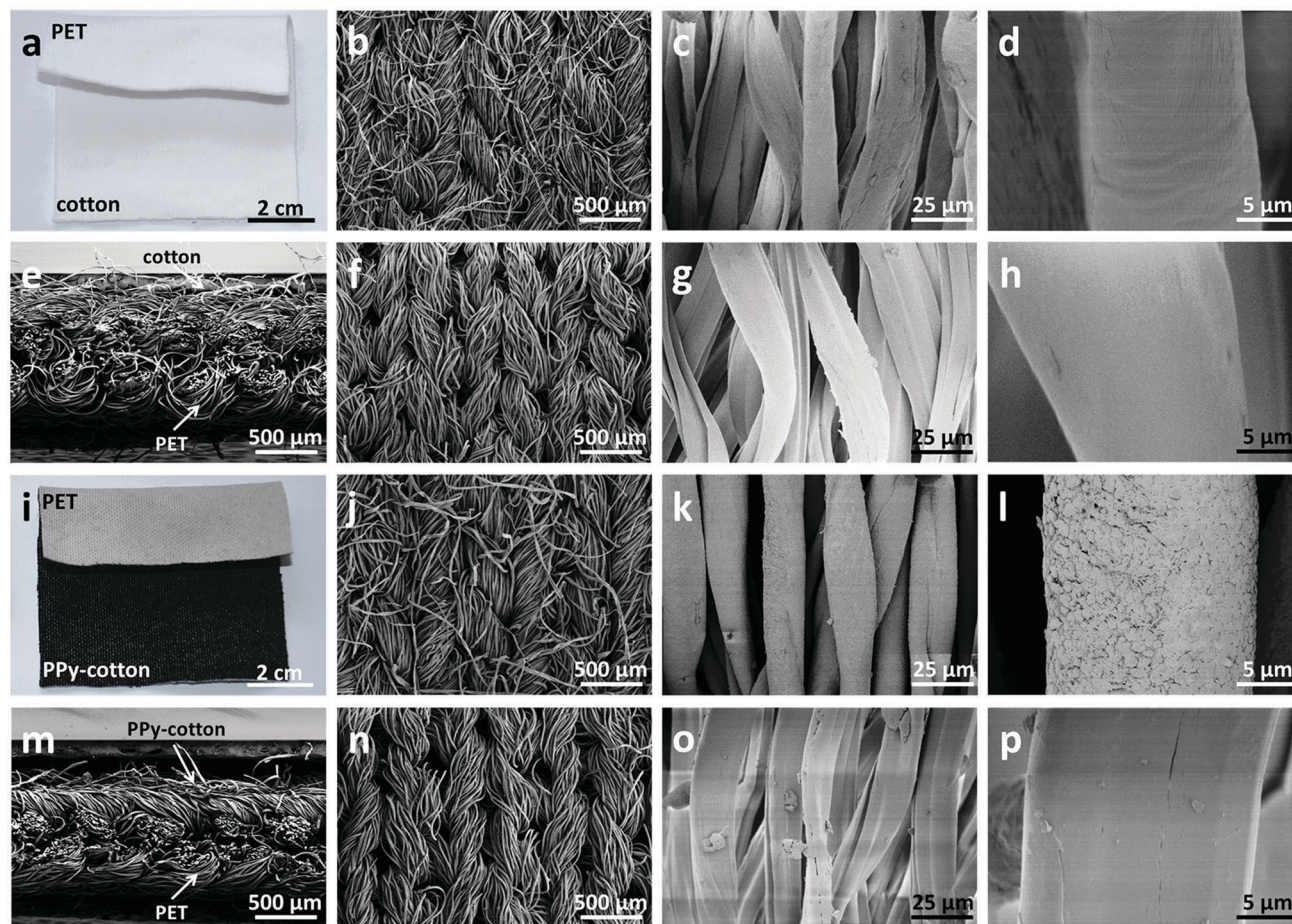
**Fig. 1** (a) Photograph of a blank fabric. (b–d) SEM images of the cotton side of the blank fabric with increasing magnification. (e) Cross-sectional SEM image of the blank fabric. (f–h) Polyester side of the blank fabric with increasing magnification. (i) Photograph of a single-sided conductive fabric. (j–l) SEM images of the cotton side of the single-sided conductive fabric with increasing magnification. (m) Cross-sectional SEM image of the single-sided conductive fabric. (n–p) Polyester side of the single-sided conductive fabric with increasing magnification.

electrical conductivity, stability, processability and flexibility, conducting polymers are well suited for the fabrication of conductive textiles.[23–27] Commonly, PPy can be coated on the fabric through the *in situ* polymerization of pyrrole monomers initiated by FeCl$_3$, accompanied with NaAQS as a dopant.[28,29] It is not surprising that the fabric completely turned black after the reaction since the cotton and polyester fibers were simultaneously covered with PPy conductive aggregates (Fig. S1, ESI†). However, the colors painted on dark cloth with thermochromic inks become difficult to identify by virtue of the reduction of reflected light (Fig. S2a, ESI†). Moreover, the dark color of the conductive layer restricts the color diversity of the fabric. Therefore, a light-colored conductive substrate should be developed for the preparation of smart color-changing fabrics.[30]

Interestingly, when FeCl$_3$ was substituted with APS as the oxidant, accompanied with SDS as the dopant, PPy was selectively grown on the cotton side of the fabric while the polyester side remained white after *in situ* chemical oxidative polymerization (Fig. 1i). Compared to the blank fabric substrate, each individual cotton fiber of the conductive fabric exhibited a rough surface that was entirely covered with PPy particles (Fig. 1j–l). As for the

polyester fiber, only very few scattered particles were observed (Fig. 1n–p). PPy can be deposited on polyester fabric using APS as oxidant in the presence of non-ionic surfactant or non-surfactant dopants.[31–33] So we deduced that the selective growth of PPy on the cotton fiber was attributed to SDS, which is an anion surfactant. It is known that polyester fiber is hydrophobic while cotton fiber is hydrophilic. Due to hydrophobic interactions, polyester fibers should be protected by SDS and possess negative charges in aqueous solution. The negatively charged group of SDS would effectively prohibit the persulfate anion to initiate the polymerization of pyrrole monomers on the surface of polyester fibers. These results present a very facile and low-cost approach to obtain single-sided conductive substrates with a light color.

The surface resistivity of the conductive fabric was measured, showing an average value of 134 Ω sq$^{-1}$ from 12 samples. The variation of the electrical resistance of these conductive fabrics was then investigated during the mechanical stretching process. When the fabric was stretched in the range of maximum strain along the course or wale direction, the electrical resistance continued to decrease (Fig. S3, ESI†). This could be attributed to the better surface–surface contacts within the conductive yarns

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under stretching, which reduced the contact resistance and enhanced the conductivity.[34] Furthermore, the electrical resistance of the fabric after 1000 stretching cycles at a strain of 10% was almost the same as the first stretching cycle, revealing high flexibility and stretchability (Fig. S4, ESI†). The conductive layer was coated on an individual fiber, and the elasticity of the knitted fabric was derived from the meandering loops rather than fibers, therefore higher elastic conductivity fabrics can be easily obtained by changing the knitting pattern. The air permeability value of the conductive fabric was $33.2 \pm 0.7$ mm s$^{-1}$, which was lower than that of the blank fabric ($54.5 \pm 0.7$ mm s$^{-1}$). The abrasion resistance of the fabric was also tested (Fig. S5, ESI†). After 100 abrasion cycles, the surface resistivity of the fabric was not obviously increased, revealing a good resistance to abrasion. These properties are critically important to guarantee the effect of resistive heating and stability of the smart fabric during use.

The resistive heating properties of the conductive fabric were studied by applying different currents to a piece of sample and recording the temperature changes of the polyester side after a duration of 1 min using an infrared camera. A uniform evolution of heat on the surface of the conductive fabric was observed (Fig. 2). The temperature of the fabric did not differ too much from the ambient environment at 30 mA since the current could be efficiently transported through the PPy conductive coating. With the increase in current, the excess electrical energy was transformed into heat energy to increase the temperature of the conductive fabric gradually.

The temperature of a circular region with a diameter of 5 mm located at the center of the sample was further monitored as a function of the applied current (Fig. 3a). Below 30 mA, a slight temperature increase was detected. When the current exceeded 30 mA, the temperature of the fabric began to increase drastically and reached over 70 °C at 150 mA. This impressive temperature increase was ascribed to the remarkable electric conductivity of the PPy coating and heat dissipation of the polyester fibers. The obvious correlation between the current and the temperature reached provides the possibility to obtain the desired heat evolution by adjusting the input current. At a current

value of 150 mA, the voltage was 20 V and the power was then 3 W. The heat dissipation area of the sample is 10 cm$^2$, so the heating power can reach over 3000 W m$^{-2}$, which is higher than other reported resistive heating textiles based on PPy.[35–38]

Afterwards, the heating/cooling cycling stability was investigated. The temperature change of the conductive fabric was recorded over a period of 2 min (heating 1 min at 120 mA and cooling 1 min at 0 mA). As shown in Fig. 3b, the heating/cooling curve remained almost unchanged after 120 cycles, indicating good stability and repeatability. During each heating process, the temperature increased from room temperature to over 50 °C in the initial 10 s, revealing a very high heating rate of the PPy conductive coating. Due to the heat preservation function of cotton fibers, the heat dissipation of the fabric was relatively slow once the power was off.

The evolution of heat with time was studied (Fig. 3c). The conductive fabric was subjected to successive heating at a constant current of 120 mA over a period of 2 h. It was found that the surface temperature of the fabric increased quickly and then stabilized in a narrow region ($68 \pm 3$ °C) over the whole duration. The fluctuation of the temperature is probably ascribed to the fact that the electron flow at fiber junctions undergoes multiple separations/recombinations, leading to a dynamic balance at each point in the fabric.[20] So far, this light-colored conductive fabric has displayed remarkable resistive heating properties, which are suitable for color-changing heating garments or heating pads.

A smart color-changing fabric was then constructed based on this light-colored conductive fabric. Thermochromic inks were painted on the surface of the polyester side by screen printing, which is a widely used printing technique in the textile industry. The thermochromic ink formed a coating on top of the polyester side excluding the gaps among the fibers (Fig. 4a). Due to the double-faced structure, the thermochromic ink did not penetrate into the cotton side, as shown in the cross-section of the fabric (Fig. 4b and c). The thermochromic ink used here has a colored state at low temperature and a transparent state at high temperature. The transition temperature is 45 °C in order to eliminate any color transition caused by
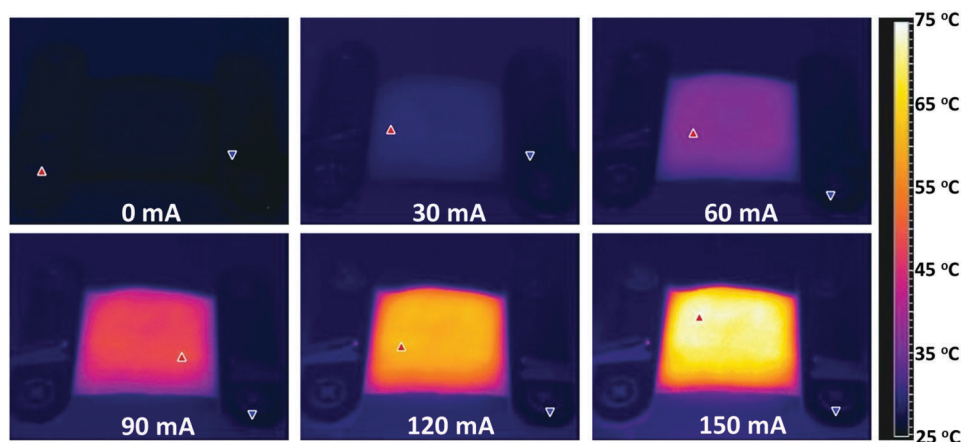


Fig. 2 Infrared thermal images of the polyester side of the single-sided conductive fabric (3.5 cm × 3.3 cm) at increasing applied currents.

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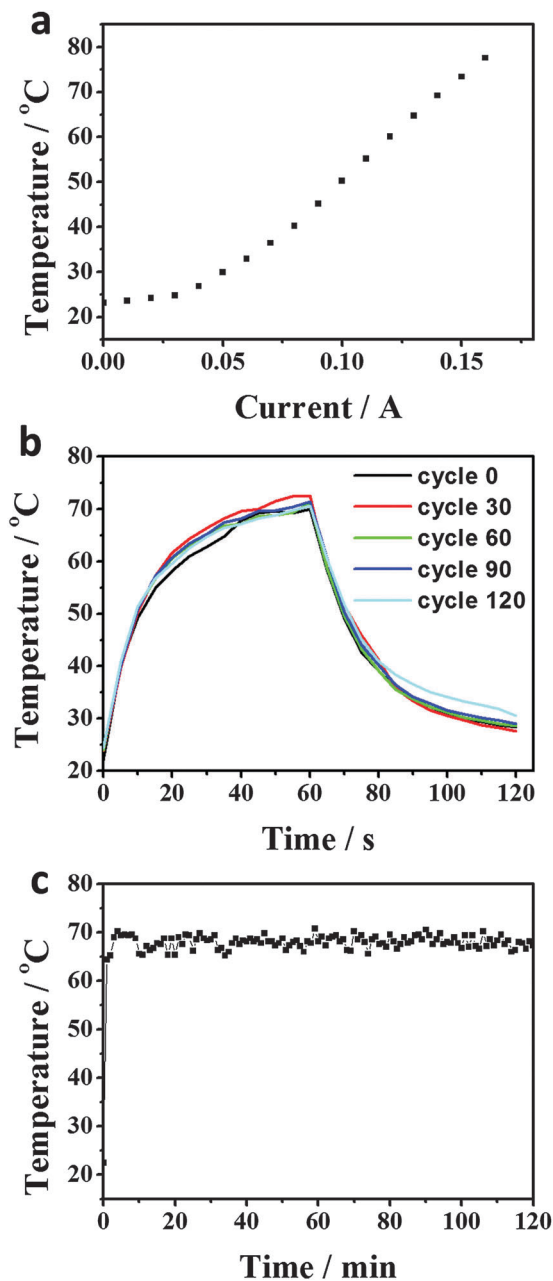This journal is © The Royal Society of Chemistry 2016

Fig. 3 (a) Plot of temperature *versus* applied current. (b) Temperature cycling stability during 120 repetitive cycles (60 s at 120 mA followed by 60 s at 0 mA). (c) Time/temperature curve at a constant current of 120 mA.



Fig. 4 (a) Cross-sectional SEM image of a smart color-changing textile. (b and c) Polyester and cotton side of the textile after painting with thermochromic ink, respectively. (d) Photographs of the textile (3.6 cm × 3.5 cm) showing smart color-changing effect by applying currents of 120/0 mA.

color contrast was displayed on the light-colored conductive fabric. However, the color of the letters on the black conductive fabric is difficult to distinguish before and after the color change.

The color-changing properties of this new smart fabric were examined by applying a certain current. When the fabric was subjected to a current of 120 mA, the temperature increased gradually so that the letters "F" and "D" turned from blue and green to colorless (Fig. 4d and Videos S1 and S2, ESI†). Once the power was off, the letters gradually turned back to their colorful state. The color-changing process could be repeated thousands of times thanks to the great heating/cooling cycling stability of the conductive fabric and the color reversibility of the thermochromic inks. By adjusting the applied current or choosing thermochromic inks with other transition temperatures (*e.g.*, 37 °C), the transition time of the color could be varied. The aforementioned results revealed that the heat was uniformly distributed on the surface of the conductive fabric; therefore any other pattern could be painted on the fabric as needed. Apart from the pattern, the color change could also be adjusted to display more abundant variations, depending on the color and color-changing types of thermochromic inks (*e.g.*, changing from a colored state at low temperature to another colored state at high temperature).

## Conclusions

In summary, a smart color-changing fabric was prepared *via* a simple and low-cost approach on the basis of a single-sided conductive fabric substrate with light color. The conductive substrate was produced by the selective deposition of PPy on the cotton side of a polyester-covered cotton fabric. The high conductivity of the PPy coating gave the fabric great resistive heating properties, including rapid heating performance and remarkable stability. Thanks to the light color of the conductive substrate, patterns painted on the polyester side using thermochromic inks could undergo color changes with bright color contrast under the control of electricity. The smart color-changing

the change of environmental conditions. To further demonstrate the significance of the base color for the effect of color change, black conductive fabric was used to compare with this light-colored conductive fabric. Three letters of 'R', 'G' and 'B' with the corresponding three primary colors were painted on two fabrics using different thermochromic inks (Fig. S2, ESI†). Apparently, the colors of the letters on the black fabric looked darker than those on the light-colored fabric, especially for green and blue. As shown in Fig. S2b (ESI†), the color of the letters faded when the fabrics were heated to exceed the transition temperature of the thermochromic ink. A bright
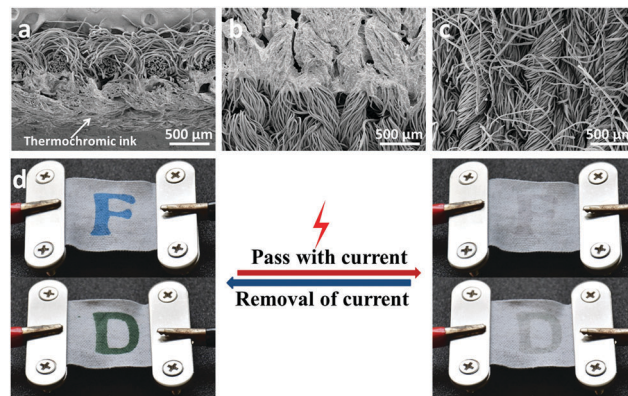
properties of the fabric ensure its potential applications in next-generation wearable devices, such as active visual camouflage or interactive textiles. This work also presents a general and effective approach for developing high-performance resistive heating textiles.

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