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Red, Green, Blue (RGB) Electrochromic Fibers for the New Smart Color Change Fabrics

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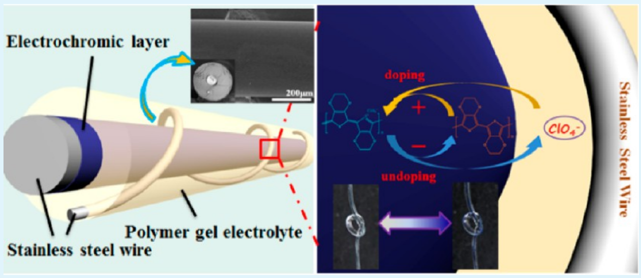
Supporting Information



ABSTRACT: These fibers are prepared using stainless steel wires (SSWs) as a substrate. Three kinds of electrochromic materials (poly(3,4-ethylenedioxythiophene), poly(3-methylthiophene), and poly(2,5-dimethoxyaniline)) are quickly deposited on the surface of the SSWs by electrochemical polymerization. A polymer gel electrolyte is then coated onto the electrochromic layer, and another finer stainless steel wire is twisted on, in succession. The obvious RGB colors and gradient color phenomenon from gray to dark blue are observed by the naked eye besides color changes from oxidized to reduced states. Moreover, these electrochromic fibers have very short response times (millisecond scale), excellent flexibility, and good structural stability even though the bending and folding occurred. They also can be implanted into fabrics to achieve more color combinations through regulating the voltages and parallel connection of different circuits.

KEYWORDS: *electrochromic fibers, three complementary colors, gradient color phenomenon, π-conjugated organic polymers, smart fabrics*

1. INTRODUCTION

The importance of the colors is self-evident. Thanks to various colors endowing the materials with more features, we human beings can live a colorful life. It is well-known that fibers, as one kind of distinctive one-dimensional material, have always been applied in the textile field and very closely related to people's daily lives. Nowadays, increasing amounts of multifunctional devices and materials have been studied on fiber substrates or in the form of fibers,[1−8] which can be integrated into the fiber products perfectly. How to achieve functionalization and intelligence of fiber colors has increasingly become an urgent problem.

In recent years, smart color change fibers have become a hotspot, due to their potential application in various areas, such as wearable displays, sensors, camouflage, anticounterfeiting techniques, and even the military industry. Traditionally, the fiber colors prepared by dyeing and finishing techniques cannot be smartly changed. Thus, a series of recent studies have focused on fibers or fabrics that have controlled colors using the new approaches and methods.[9−14] Liu et al. fabricated structural colored fibers where color change is possible by controlling the size and layers of silica nanospheres by self-assembly in the microspace.[10] Laforgue et al. prepared a thermochromic fiber, and color change was obtained upon resistive heating.[11] However, these fibers still have many shortcomings and disadvantages, such as quite a long switching time, few color changes, high energy consumption, and so on. Therefore, it is very important to find a suitable way to change and control the fiber colors.

To change the color of fibers, voltage is an easily and efficiently controlled factor. Using low voltage to drive color change is very convenient and effective in giving a fast color change to the required color. Therefore, the electrochromic materials provide a new direction for this color change approach. Considering that traditional electrochromic devices always use a plane rigid or flexible substrate to build a sandwich structure,[15−20] it is difficult to fabricate these devices in the one-dimensional form. At present, very few reports exist about fibrous electrochromic filaments. A few studies exist about electrochromic monofibers using carbon nanotube/polydiacetylene nanocomposite fibers as reported by Peng et al.[12] However, the color change only lasts 2 s after the removal of the current. This is because the color change in these fibers is caused by a conformational change of polydiacetylene as a result of stimulation by current. Moreover, this fiber color will be easily changed under various external stimuli (temperature, pH, mechanical stress, etc.), which may influence the electrochromic effect and cause irreversible color change. What's worse, owing to limited types, this kind of electrochromic material has only a few colors to change, far less than

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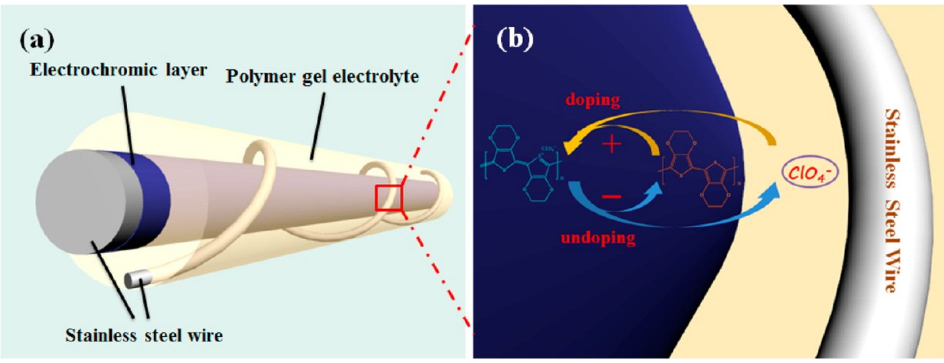

Figure 1. (a) Structure diagram of the electrochromic fibers. (b) Electrochromic mechanism of the fibers with PEDOT as electrochromic layer.

meeting application needs. Therefore, it is very necessary to prepare the multicolored fibers with high controllability, good optical properties, fast switching speed, and low energy consumption.

It is well-known that π-conjugated organic polymers can be used as electrochromic materials because of their excellent properties such as mechanical flexibility and ease of bandgap/color tuning by structural control, and they potentially offer low-cost scalability and processing.[21] Having three complementary colors (red, green, and blue) constitutes an important step forward to the use of conducting polymers in polymeric electrochromic devices (PECDs),[22] and many people are committed to developing three new complementary color electrochromic devices with better performance. However, according to our knowledge, there are no people having reported RGB tricolor electrochromic fibers that can be seen by the naked eye.

Poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3-methylthiophene) (P3MT), and poly(2,5-dimethoxyaniline) (PDMA) are three π-conjugated organic polymers that have been studied and used as electrochromic materials. They can reversibly switch between sky blue and dark blue (PEDOT), blue and red (P3MT), and green and yellow (PDMA),[23] respectively, which form RGB electrochromic materials. Additionally, PEDOT offers different tones of blue under different reduction states.[22] In this paper, they were used as electrochromic layers and SSWs as the conductive substrate with diameters of either ca. 0.3 or 0.1 mm. Electrochromic fibers were assembled by coating with a layer of GPE (Figure 1a). Many data were provided to prove and show the RGB colors and gradient color phenomenon, including digital photographs, reflectance spectra, and simulated colors according to the RGB color values. These electrochromic fibers have all the characteristics that are described above on the plane substrate (obvious gradient color phenomenon and RGB colors) and many other excellent properties, such as fast switching speed (the millisecond range), good flexibility, and long color retention. They also can be implanted into fabrics to achieve more color combinations through regulating the voltages and parallel connection of different circuits. We think that these electrochromic fibers will expand more directions for multifunctional applications of fibers.

2. EXPERIMENTAL SECTION

Reagents and Materials. H_3PO_4 (≥85%) and PVA-1750 ± 50 (≥99%) were purchased from Shanghai Chemical Reagent Plant. Poly(methyl methacrylate) (PMMA, M_w = ~996 000 by GPC) was purchased from Sigma-Aldrich Chemicals. All other chemicals and reagents were purchased in the highest grade commercially available and used without further purification. Aqueous solutions were prepared with ultrapure water (UPW, 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA, USA) unless stated otherwise. Stainless steel wires with different diameters were all purchased from Shanghai Yongtai Electrical Equipment Engineering Co., Ltd. The different diameters of stainless steel wires (SSWs) were as follows: ca. 0.3 mm (S-1), 0.1 mm (S-2), 0.05 mm (S-3), and 0.02 mm (S-4). PMMA was dried at 100 °C for 24 h under vacuum, and SSWs were cleaned using acetone, ethanol, and deionized water sequentially before use.

Preparation of the Electrochromic Layers. Electrochemical polymerization was carried out with a potentiostat employing stainless steel wires as the working electrode, a platinum flat (1 cm × 1 cm) electrode as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The PEDOT electrochromic layer was electropolymerized in PC (propylene carbonate) solution containing 0.04 M EDOT monomer and 0.1 M $LiClO_4$. S-1 and S-2 were placed vertically in the bath, and electrochemical polymerization was undertaken at 1.3 V/8 s and 1.3 V/5 s, respectively. S-1 and S-2 were then coated with PEDOT and then rinsed with deionized water and ethanol and dried under vacuum at 45 °C for 2 h (obtaining SP-1 and SP-2, respectively). P3HT and PDMA electrochromic layers were electropolymerized and postprocessed following a similar procedure for the preparation of the PEDOT layer (then obtaining SP-3 and SP-4, respectively) except for the electrolyte and electropolymerized voltage and time required. The P3HT layer was electropolymerized in PC solution containing 0.1 M 3-methylthiophene (MeTh) monomer and 0.1 M $LiClO_4$ with an applied voltage of 2.2 V for 4 s, whereas, for PDMA, the electrolyte was 0.04 M 2,5-dimethoxyaniline (DMA) and 0.5 M H_2SO_4 aqueous solution and the parameter of electrochemical polymerization was 1.1 V/70 s.

Assembly of the Electrochromic Fibers. SP-1, SP-2, SP-3, and SP-4 were used as working electrodes and two finer SSWs (S-3 or S-4) were used as the counter electrodes to assemble four types of electrochromic fibers (EF-1, EF-2, EF-3, and EF-4). The EF-1 was fabricated by dip-coating a layer of GPE on the surface of SP-1, and then S-3 was correspondingly twisted around SP-1. Finally, we dip-coated GPE a second time and dried it at room temperature for 12 h. These steps are illustrated in Scheme S1 (Supporting Information). The polymer gel electrolyte contained 20 mL of 1 M $LiClO_4$ in PC solution and 25 wt % PMMA (relative to the $LiClO_4$ solution) in addition to 30 mL of acetone (GPE-1). EF-2, EF-3, and EF-4 were also assembled as described above, but S-4 was used as the counter electrode and the gel electrolyte required for EF-4 contained 1 g of PVA, 1 g of H_3PO_4, and 8 g of H_2O (GPE-2).

Characterization Techniques. The morphology and microstructure of the as-prepared electrochromic fibers were characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-4800) and scanning electron microscopy (SEM, Phenom-Word BV, G2pro). The reflection spectra of SP-1, SP-2, SP-3, and SP-4 were measured using a fiber-optic UV−vis spectrometer (PG2000-Pro-Ex, Ideaoptics Technology Ltd., China). Electrochemical measurements

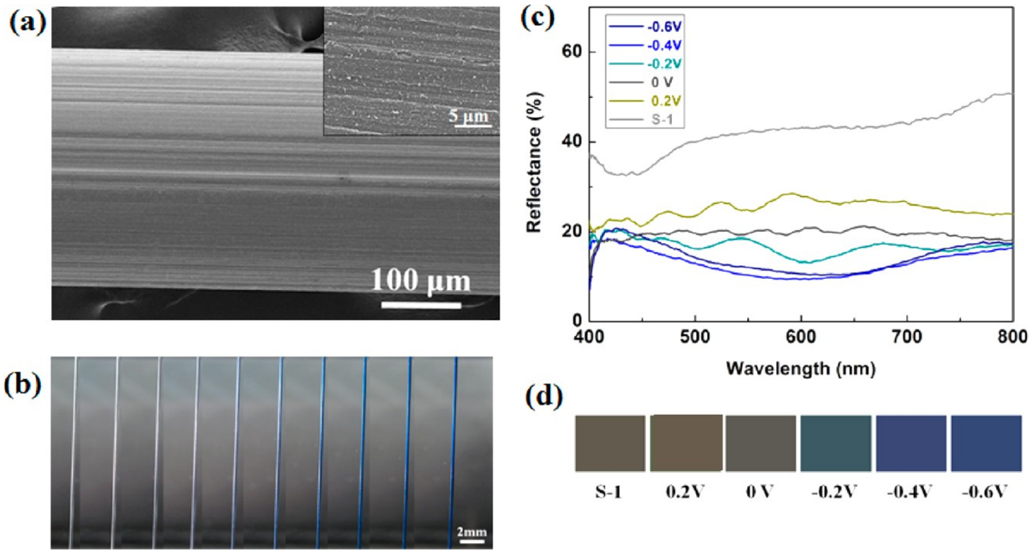

Figure 2. (a) FE-SEM image of SP-1. (b) Digital photographs of the gradient color phenomenon. Reflectance spectra (c) and simulated colors (d) of the blank stainless steel wire (S-1) and SP-1 at voltages of 0.2, 0, −0.2, −0.4, and −0.6 V, respectively.

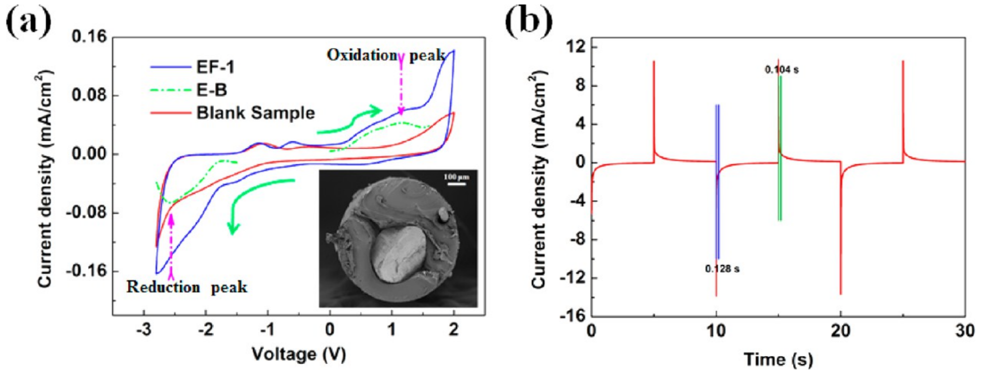

Figure 3. (a) Cyclic voltammetry curves of EF-1 and a blank sample (illustration of cross-sectional view of EF-1). (b) Multiple potential steps of EF-1 at voltages of −2.6 and 1.6 V.

were carried out using an electrochemical workstation (CHI760D, Shanghai Chenhua Instruments, China) containing a three-electrode system, which consisted of an SP-1, SP-2, SP-3, or SP-4 working electrode, and an S-3 or S-4 counter and reference electrode.

3. RESULTS AND DISCUSSION

In this work, the experimental parameters and technology were controlled to prepare a uniform thin electrochromic layer on a curved stainless steel wire surface. Unlike transparent conductive glass, SSWs themselves have color and their surface is not smooth, which will have an impact on the colors of electrochromic materials. Figure 1b is a schematic diagram of the electrochromic mechanism of PEDOT in the fibrous form. When a positive voltage is applied, the PEDOT on the surface of the stainless steel wires is doped with perchlorate ion from the GPE and becomes sky blue. Upon stimulation by negative voltage, the PEDOT becomes dark blue in the undoped state. This two-electrode structure allows color change under positive and negative voltages. The mechanisms of other electrochromic fibers are similar to the fiber using PEDOT as electrochromic layer so that we will not repeat them here.

Electrochromic Fiber with Gradient Color Phenomenon. Gradient color effect is very important and meaningful for creating diverse colors via a combination of different color tones and quantitative expression of voltage magnitude. In order to obtain the gradient color phenomenon that is visible to the naked eye on the fiber surface, relatively thicker SSWs (0.3 mm) were used to produce electrochromic fibers. At higher voltage, the deposition of PEDOT occurs in a relatively short time and a very uniform film (Figure 2a) can be obtained. Here, the gradient color phenomenon of SP-1 (the meanings of all abbreviations like this can be found in the Experimental Section) varies between gray and dark blue (Figure 2b) under the application of potentials in a stepwise manner from 0.2 to −0.7 V by a three-electrode electrochemical cell with 1.0 M lithium perchlorate ($LiClO_4$) in propylene carbonate (PC) as the electrolyte. SP-1 was retrieved from the electrolyte and quickly measured by the fiber-optic UV−vis spectrometer. Reflectance spectra at different voltages (Figure 2c) and RGB color values were obtained using supporting software. The corresponding colors (Figure 2d) were simulated for each spectrum using the obtained RGB color values. The simulated colors show a little difference from that in digital pictures, because the imaging process is affected by complicated external conditions, including light intensity, angle of incident light, and so on. However, a significant color gradient was still found for the simulated colors. According to the literature, PEDOT ought to be sky blue rather than gray in the oxidation state.[22] This is because the PEDOT layer is thin so that the background color

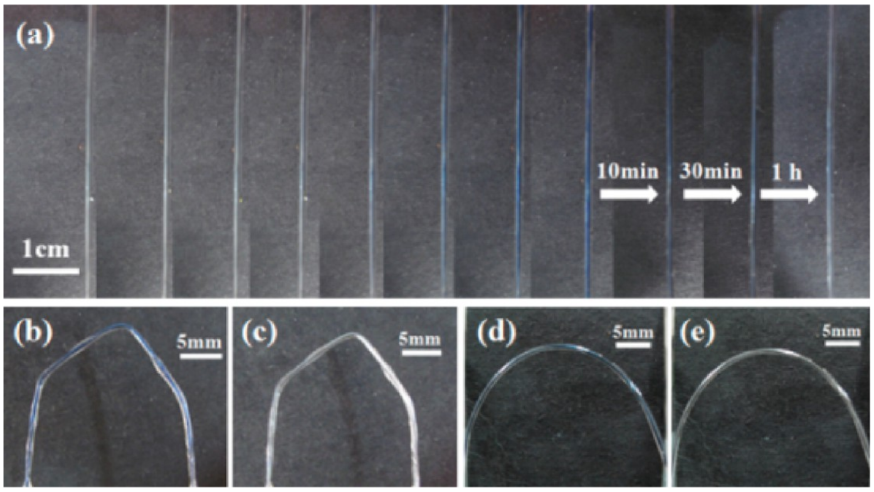

Figure 4. (a) Digital photographs showing color gradients at voltages of 1.6, 0, −1.6, −1.8, −2.0, −2.2, −2.4, and −2.6 V and an optical memory effect after 10 min, 30 min, and 1 h. Electrochromic effect at voltages of −2.6 (b, d) and 1.6 V (c, e) after folding and bending.

of the SSWs shows through the PEDOT layer and influences the fiber color. However, when PEDOT is reduced, the deep blue PEDOT will completely cover the color of SSWs. Many reflection spectra of fibers have some small serration or waves instead of smooth curves. This is because there are many strip-shaped sags and swells with different widths along the axis of the fiber, as shown in Figure 2a, which lead to scattering and interference of reflected light in some positions.

Here, the solid-state electrochromic fibers were assembled as shown in Scheme S1. SEM images of the surface and a cross section of EF-1 (Figure S1, Supporting Information) prove its double-electrode spiral winding structure. Figure 3a shows cyclic voltammetry curves of EF-1 and a blank sample where the scan range is −2.8 to 2.0 V at a scan rate of 100 mV/s. The redox potentials of EF-1 can be obtained through these curves. The oxidation and reduction of PEDOT comes from ion doping and undoping. However, with the addition of PMMA, the conductivity decreases[24] and ion movement is hindered by the polymer in the gel electrolyte. Therefore, the voltage required for color change is significantly higher than the voltage in the liquid electrolyte. With an increase in voltage, the ions gradually move toward and dope/undope with PEDOT instead of undergoing quick movement and a redox reaction in the liquid electrolyte. When a higher voltage is applied, there occurs the redox reaction between GPE and the SSW. Therefore, the redox peaks of PEDOT and some other peaks were observed. An assembled fiber without a layer of PEDOT (blank sample) was also subjected to cyclic voltammetry, and peaks were found at potentials around −2.8, −1.1, −0.4, and 2.0 V in the cyclic voltammetry curve. These peaks correspond with some previously observed peaks and prove that they are not the redox peaks of PEDOT. In order to further determine the redox peaks, the CV curve of EF-1 was used to deduce the curve of the blank sample in the position of around redox peaks (obtaining the green curve (E-B) in Figure 3a). Redox peaks can be easily found at ca. 1.2 and −2.5 V. The arrows indicate the position of the redox peaks in the curve.

The switching speed from one state to another state is an important property in electrochromic devices. The response time is the time taken for the current density to drop to 10% of the maximum value.[9,25,26] The response time of EF-1 was determined using multiple potential steps (Figure 3b) at voltages of −2.6 and 1.6 V. Calculated coloring and bleaching times of EF-1 were 0.128 and 0.104 s, respectively. The switching speed of EF-1 is quite fast in the millisecond range. Therefore, their application value is high especially in quick displays and camouflage.

We previously discussed the gradient phenomenon of PEDOT in a liquid electrolyte. The assembled electrochromic fibers should still have an obvious gradient when voltage is applied in a stepwise manner between 1.6 and −2.6 V. When the voltage is applied from 1.6 to −1.6 V, the color does not change because there is no ion undoping and appearance of a reduction peak through the cyclic voltammetry curve of EF-1. However, the blue color gradually appears when a potential higher than −1.8 V is applied. Up to −2.4 V, the color is saturated and no darkening occurs. The digital photographs in Figure 4a clearly show this gradient process. When the voltage is removed, PEDOT has an optical memory and the dark blue color is still obvious at 30 min. This is because the polymer hinders the doping and movement of perchlorate ion. EF-1 still has a good electrochromic property after the folding and bending of EF-1 (Figure 4b−e) when voltages of −2.6 and 1.6 V are applied, respectively. This proves that, when folding or bending occurs, there is no direct contact between the two electrodes, which would cause short-circuiting, and the electrodes do not separate from the electrolyte. The wound structure of the electrochromic fibers is not damaged and has good stability.

RGB Tricolor Electrochromic Fibers. Color is the indispensable function for the fibrous materials and devices. To prepare a weavable electrochromic fiber with a variety of color changes, the diameter of the stainless steel wire has to be reduced and different electrochromic materials must be used. Here, 0.1 mm SSWs were used as the substrate. With a reduction in the diameter of electrochromic fibers, its flexibility is greatly improved. Three electrochromic materials were deposited on the surface of SSWs using electrochemical polymerization. SP-2 (Figure 5a) has the similar color change with SP-1 besides showing blue gray under the oxidation state. SP-3 and SP-4 are shown between red and dark blue (Figure 5c), and yellow and green (Figure 5e) when different voltages were applied by a three-electrode electrochemical cell with 1.0 M $LiClO_4$ in PC and 0.5 M H_2SO_4 aqueous solution as the electrolyte, respectively. Sulfuric acid aqueous solution was used for electrochemical measurements of SP-4. Because PDMA

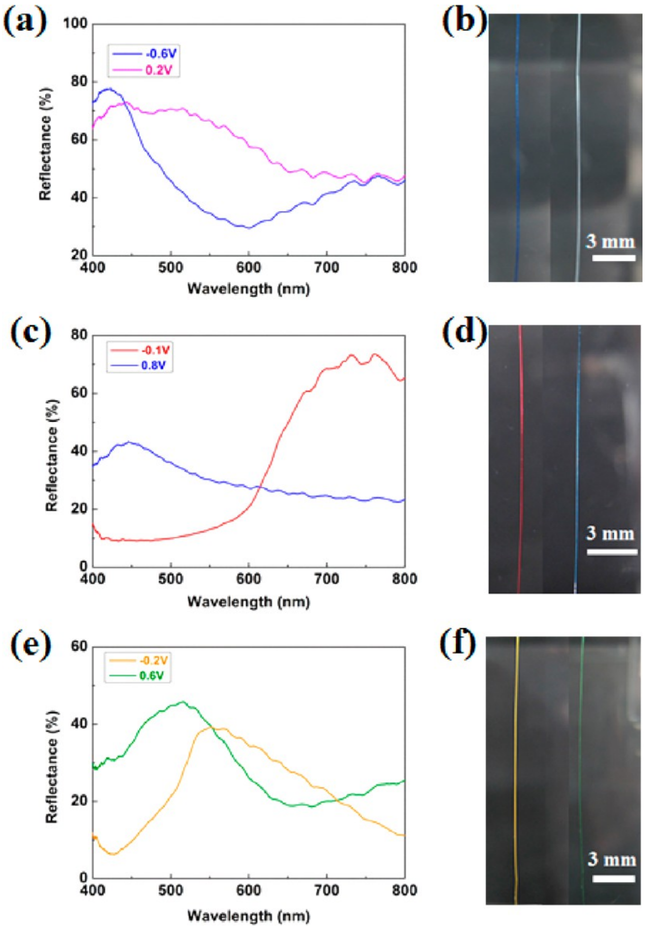

Figure 5. Reflectance spectra of SP-2 (a), SP-3 (c), and SP-4 (e) at different voltages. Corresponding digital photographs (b, d, f) under reduced (left) and oxidized (right) states.

would dissolve in a PC solution of $LiClO_4$. This situation also leads to unsuitability of using this solution as a composition of GPE to assemble EF-4. Through digital photographs and reflectance spectra of fibers, their color changes can be clearly detected. Here, we not only obtained red, green, and blue colors (three complementary colors) but also got the yellow color.

RGB electrochromic fibers were assembled using the same process as that of EF-1 (Scheme S1) so that they have the same structure as the EF-1 (Figure 6a). Because of the far distance between PDMA and the electrode caused by dissolution and diffusion of PDMA, the color of PDMA cannot be changed when EF-4 was assembled using the GPE-1. Here, the GPE is replaced with acid solution and PVA to assemble EF-4, because the electrochromism of PDMA is doping and undoping of hydrogen ions.[23] At the same time, in order to avoid the volatilization of water leading to an increase of concentration of H_2SO_4 that probably damages the electrochromic layer, H_3PO_4, which has a much lower causticity and oxidation, is used instead of H_2SO_4 in GPE. Through cyclic voltammetry curves (Figure 6b−d), redox potentials of these electrochromic fibers can be clearly found. However, EF-2 and EF-3 have some other small peaks besides the redox peaks, which is in the same situation as EF-1. This is because there exists the redox reaction between electrolyte and substrate (SSWs) at the high positive and negative voltages. The response times of EF-2, EF-3, and EF-4 were calculated via the multiple potential step curves (Figure 7a,c,e), and these were 0.446 and 0.278, 0.018 and 0.026, and 0.016 and 0.012 s, respectively. The switching speeds are so fast that EF-3 and EF-4 just need tens of microseconds to complete the color changes. We consider that this is because of good conductivity of SSWs and the unique spiral winding structure of electrochromic fibers. Although they appear darker than unassembled fibers due to the influence of GPE on reflectance of light, obviously the electrochromic performance can still be seen between dark blue and gray (Figure 7b), red and black

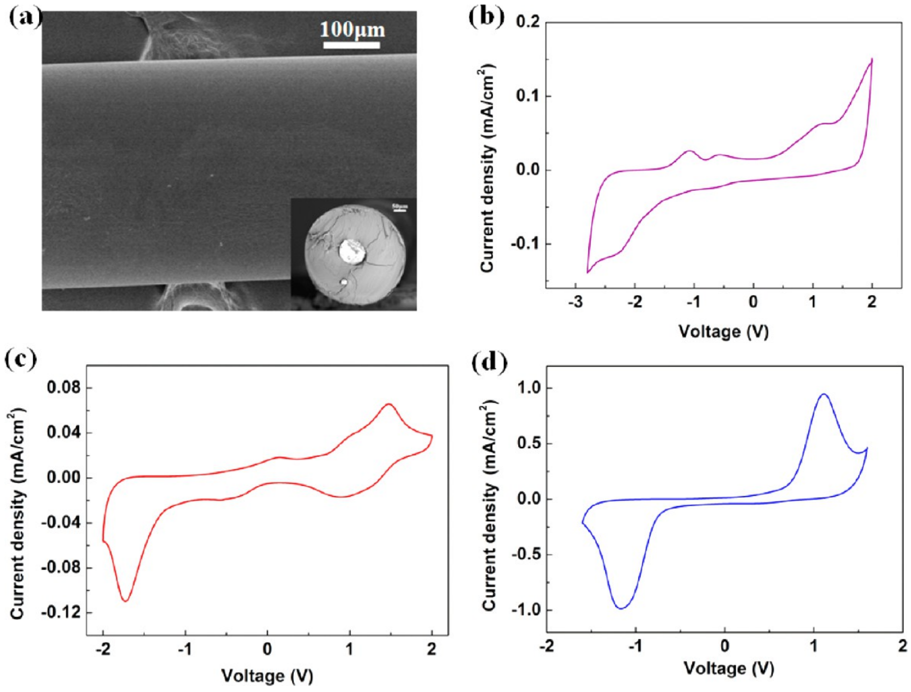

Figure 6. (a) SEM images of EF-2 (illustration of cross-sectional view). Cyclic voltammetry curves of EF-2 (b), EF-3 (c), and EF-4 (d).

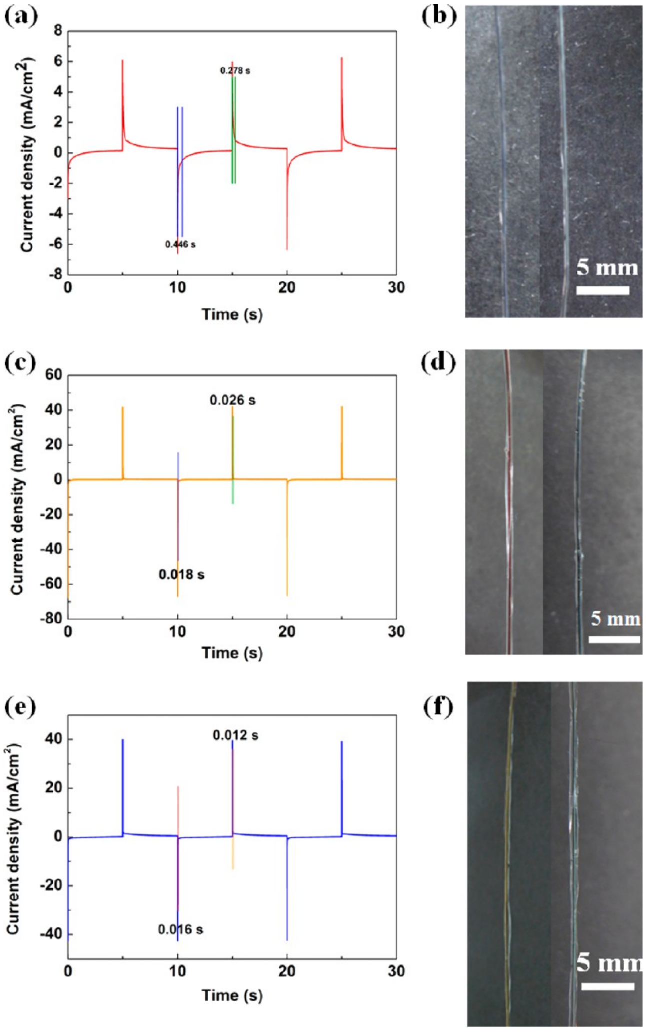

Figure 7. Multiple potential step curves of EF-2 (a), EF-3 (c), and EF-4 (e) at the voltages of −2.6 and 1.6, −2 and 2, and −1.4 and 1.4 V, respectively. Corresponding digital photographs (b, d, f) under reduced (left) and oxidized (right) states.

(Figure 7d), yellow and dark green (Figure 7f) by the naked eye. The RGB colors can also be achieved.

Digital photographs of EF-2 in various forms (Figure 8a−f) are shown before and after coloration in which no obvious decrease in color change performance was detected. EF-2 can also be woven into textile structures (Figure 8c,f) owing to its excellent flexibility. The electrochromic fibers still have good structural stability even though deformation occurs. These properties provide a basis for the application of smart fabrics.

Implantable Electrochromic Fabric. Implanting functional fibrous devices into existing fabrics is a very effective, convenient, and highly operable method, making it possible to widely use them in smart clothing. We believe that the color change effect will be greatly improved if there are more electrochromic fibers implanted together. Here, in order to test the electrochromic performance of fibers in fabrics, RGB electrochromic fibers were implanted into the warp or weft of black nylon fabric (the diameter of nylon fiber used is ca. 0.5 mm).

As shown in Figure 9a, implantable electrochromic fabric has three return circuits (C-1, C-2, and C-3) combined into the shape of "DHU", in which EF-2, two EF-3 and EF-4 are employed, respectively. When three return circuits are applied with the voltages of −2.6 and 1.6, −2 and 2, and −1.4 and 1.4 V, respectively, three letters "DHU" can change colors between dark blue and gray (Figure 9b), red and black (Figure 9d), and dark yellow and gray (Figure 9c) in succession. Then, three circuits were connected in parallel and the voltages of −3 and 3 V, respectively, were applied. Color changes of three letters (Figure 9e) occurred simultaneously. The color changes are not significant and slightly different from what is previously described, because the electrochromic fibers woven into the fabric are not in a plane and the digital camera cannot focus all the surface of fibers. However, the color changes can still be observed by the naked eye. Through regulating the voltages and parallel connection of different circuits, we can achieve many more color combinations. Therefore, it is not difficult to imagine that we can create richer color changes, if more electrochromic materials can be utilized into the fabrics in this form.

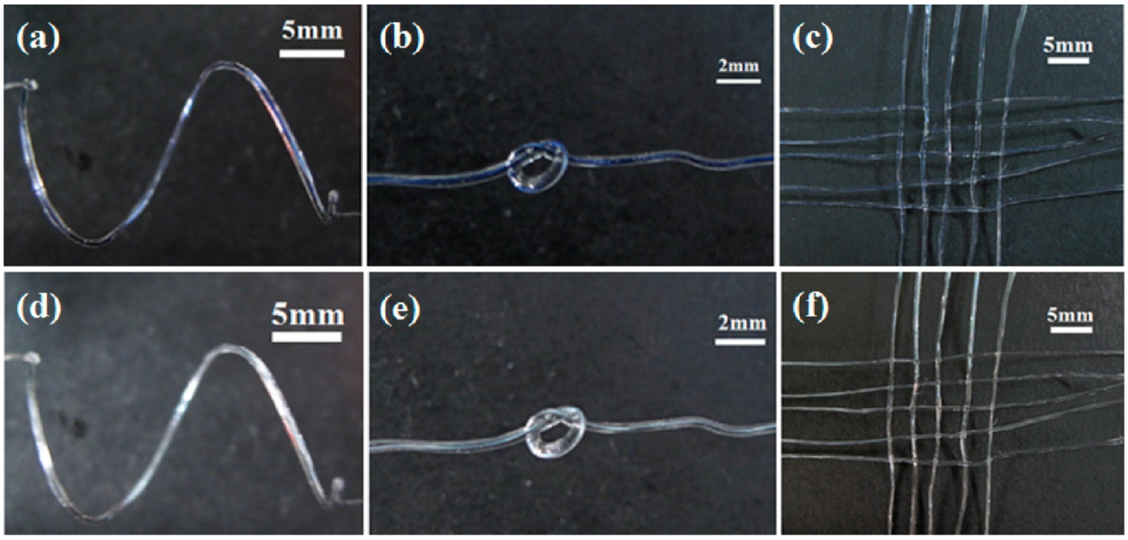

Figure 8. Electrochromic effect at voltages of −2.6 V (up) and 1.6 V (down) in spiral (a, d), knotted (b, e), and braided (c, f) forms.

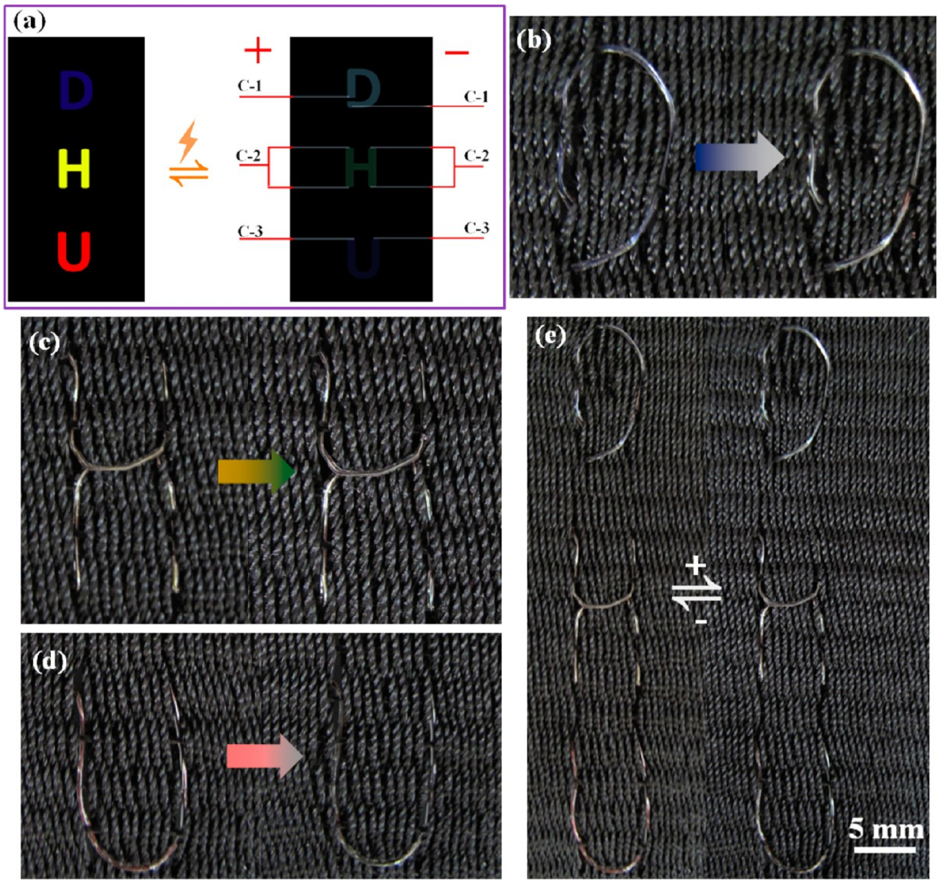

Figure 9. (a) Schematic and circuit diagram of implantable electrochromic fabric. Digital photographs of electrochromic fibers in the form of "D" (b), "H" (c), "U" (d), and "DHU" in parallel circuit (e) at negative (left) and positive (right) voltages.

4. CONCLUSIONS

In this work, gradient color effects of the electrochromic fiber using PEDOT as an electrochromic layer were observable by the naked eye, and the color can be sustained for a relatively long time (30 min) without the application of voltage. Through the utilization of three kinds of electrochromic materials, RGB electrochromic fibers were obtained for the first time. Also, their flexibility is greatly improved by reducing the diameter of SSWs, which enables them to be used for weaving and the design of patterns with several colors. Apart from these characteristics, color changes can be achieved at low voltage and with fast speed (millisecond level). The spiral winding structure of the electrochromic fibers still has good stability after the deformation.

All the excellent properties ensure their potential applications in a new generation of wearable devices. Meanwhile, these kinds of electrochromic fibers, with the application of more electrochromic materials and rapid development of integrated circuits, will be perfectly used in smart fabrics with abundant colors and high-resolution changes in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation of the electrochromic fibers (Scheme S1) and SEM images of the surface and a cross section of EF-1 (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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