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# Responsive Polymer Composite Fiber

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## What is the most favorite and original chemistry developed in your research group?

The conception and realization of display textile. Displays are the basic building blocks of electronics. Integrating displays into textiles offers exciting opportunities for smart electronic textiles, which are believed to change the future life of the human being. For instance, display textiles serve to bridge human-machine interactions, and a real-time communication tool may become true for individuals with voice or speech disorders. After hard work for over ten years, we have finally achieved this goal at lab and further produced such display textiles at large scale at industry.

## How do you get into this specific field? Could you please share some experiences with our readers?

When I started to do research independently at Fudan University, I tried to do something unique. I just did not hope to simply follow the available direction. I majored at chemical fibers during my undergraduate study and later made research on electronic devices, so it was natural for me to combine fibers and electronics together. I do not remember the detail time I figured out the idea. In my mind, it should be very interesting and must be very cool. I did not know and even had not thought whether they were useful or not. After the paper was published in 2021, so many people contacted us for the use of display textiles for a spectrum of applications. During the study on the display textiles that have been also investigated for smart systems, we started to explore new smart fiber

materials almost at the same time. These smart fiber materials are discussed in this article.

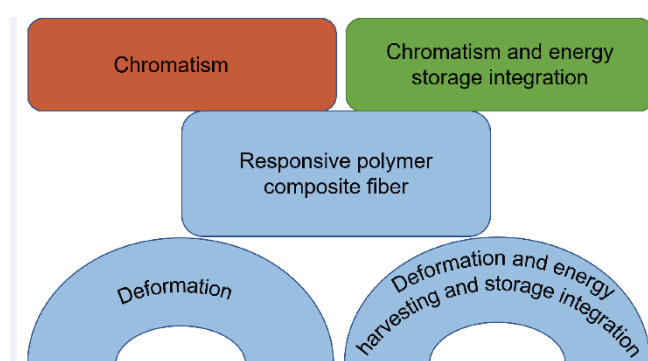
## How do you supervise your students?

First, it is important for me to understand them as every student is unique. Second, according to their characteristics, I may choose specific research projects, often following their interests. Third, I fully respect them when they start the research. They are totally free to decide the work time and work style. I trace the process mainly aiming at solving problems for them. Of course, I keep asking them to enhance their scientific tastes and make the first-class research, not only so-called original science or technology. I will try my best to help them to publish their results at top journals, which is important for their future development. During the whole training process, the most important thing I hope to achieve is enjoying science, at least feel successful. It is obviously not easy. Sometimes we make it, and sometimes we fail. We always work for the better full of hope. I sincerely hope that every student, after graduation, will have a good memory at my lab.

## What is the most important personality for scientific research?

I think there are two very important characteristics. One is brave. A scientist should be brave to solve the most difficult problem in the field. The other is imagination. Science is pretty similar to arts in many aspects. We may fix the gap sometimes through imagination. However, it is particularly challenging to train scientists for good imagination in science.

## Comprehensive Summary



Wearable devices are a mainstream for our future daily life, where responsive polymer composite fibers represent one of the key components. However, their practical applications are hampered by several challenges, including poor responsive reversibility, poor controllability and low stability as well as single function. Herein, we share our recent studies on overcoming the above challenges for achieving novel responsive polymer composite fibers, especially focusing on chromatic fibers, deformational fibers and their integrations. Furthermore, we introduce a type of novel materials for these responsive fiber materials, *i.e.*, aligned carbon nanotube sheets and fibers simultaneously with excellent electrical, optical and mechanical properties. For the future development, we further highlight the possible directions in this field.

## Keywords

Chromatism | Deformation | Polymer | Polydiacetylene | Nanotube

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## 1. Introduction

Due to their excellent properties enabled by controlled structures, responsive polymer materials have been broadly investigated in a variety of fields, *e.g.*, sensing and actuating devices.<sup>[1-6]</sup> Chromatism and deformation are two typical responsive behaviors, where polydiacetylene (PDA) and azobenzene-containing liquid-crystalline polymers (ALCPs) are major representatives, respectively.<sup>[7-8]</sup> However, their promising applications have not been realized yet due to several big challenges.

For chromatic PDA materials, there are three difficulties needed to overcome. Firstly, most PDA materials show irreversible chromatic responses.<sup>[9]</sup> For example, PDA can change its colors from blue to red easily upon increasing temperatures but the reversible process remains difficult. Secondly, PDA materials respond to limited external stimuli such as temperature, chemical and stress.<sup>[10]</sup> Thirdly, PDA materials are usually rigid with limited colors, which are not suitable for portable and wearable electronics.<sup>[11-12]</sup> Specific to the above three challenges, we proposed the corresponding solutions. To enhance the thermochromatic reversibility of PDA materials, two main modifications in side chains have been designed, *i.e.*, incorporation of stable and rigid inorganic frameworks and improvement of hydrogen-bonding interactions among the head groups of side chains in PDA. Besides, novel PDA materials responding to current, magnetic field and ultraviolet have been achieved by incorporating aligned carbon nanotubes (CNTs) and azobenzene moieties, respectively. In addition, introducing elastic fiber substrates had enabled PDA materials with both higher flexibility and stretchability, while using polystyrene photonic crystals endowed mechanochromic fibers more transitional colors of green, blue and red.

For responsive deformational materials, three critical problems remained to be solved. Primarily, ALCPs generally cannot deform reversibly under the stimuli of the same light, while it is

necessary when only one light is available or allowed.<sup>[13-15]</sup> Then, it is very hard to control the direction of deformations for responsive polymers.<sup>[16]</sup> Finally, the actuation stability and adaptability to different media are needed to be improved further.<sup>[17]</sup> Therefore, to tackle the above difficulties, we came up with corresponding methods. First of all, aligned CNT/ALCP composites have been fabricated to show reversible bending deformations under the same ultraviolet (UV) irradiation due to their interactions. Next, less responsive materials were incorporated into the responsive ones to physically constrain the deformational directions. At last, bare aligned CNTs were adopted to produce responsive actuators which are highly stable and adaptable to various media, as no electrolytes or functional guest polymers were used.

Various achievements have been realized, while functional integrations have been rarely reported although they are important for practical applications such as wearable electronics.<sup>[18-19]</sup> As a result, we proposed some new concepts, *e.g.*, new electrochromatic supercapacitors that can display real-time electric energy consumption, novel photoelectric conversion fiber *via* combining photomechanical actuation with the electrostatic effect, smart solar energy-harvesting system by integrating photodeformable actuators and fiber solar cells, and shape-memory fiber supercapacitors.

In this review article, we present a deep and concise analysis on these responsive polymer composite fibers mainly from our lab in the past decade, specifically focusing on the chromatic and deformational fibers.

## 2. Chromatism

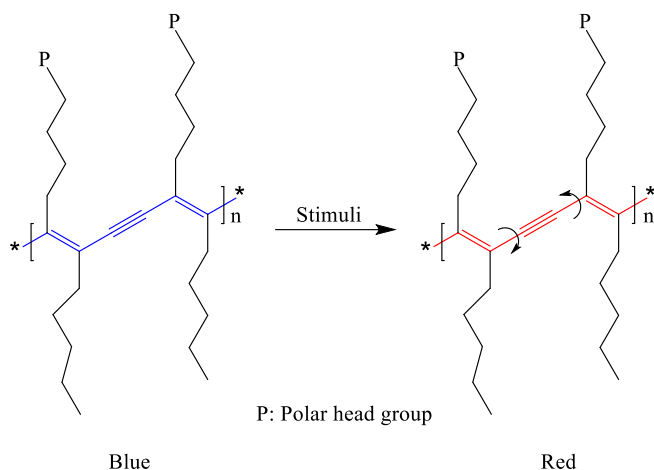
Chromatic polymers are applicable in sensing from aircraft to microelectronics, where PDA is one of the most investigated conjugated polymers.<sup>[10]</sup> The typical chromatism of PDA under external stimuli is from blue to red, which can be perceived directly using naked eyes.<sup>[20]</sup> However, their real applications are largely limited by three key challenges, *i.e.*, irreversible chromatism for most PDA materials, a limited range of external stimuli, and rigid structure and limited colors (mainly blue and red).

### 2.1. Improving thermochromatic reversibility

The chromatism of PDA from blue to red is due to the backbone conformation change induced by external stimuli. Specifically, external stimuli such as heat or stress cause fluctuations or reconfigurations of side chains and improve the rotation of the C—C bonds in backbones, which lowers the characteristic conjugation length of PDA (Scheme 1).<sup>[21]</sup> Therefore, PDA may show reversible chromatism if its backbone conformation can change reversibly, which is possible if the headgroups of side chains can

maintain stable during the environmental stimulation. Therefore, to improve the chromatic reversibility, PDA/silica nanocomposites with controllable mesostructures were synthesized by a sol-gel assembling procedure.<sup>[9]</sup> Different from the previous studies, in which the side chains of PDA interacted weakly *via* non-covalent interactions, the head groups of side chains here were covalently connected with the silica frameworks, providing stable and robust nanocomposites. Besides, due to the use of flexible side chains, the chromatic reversibility of PDA materials will increase. The hybrid structure of covalent bond also improved thermal stability of nanocomposites.

**Scheme 1** Mechanism for the chromatism of PDA from the view of molecular structure



Besides the solid PDA/silica nanocomposites, mesoporous nanocomposites were also produced through co-assembly of diacetylenic silsesquioxane with surfactant.<sup>[22]</sup> As a result, the mesoporous PDA composites could reversibly and rapidly respond to heating till temperatures up to 140 °C. Compared to the solid PDA, the mesoporous PDA could respond to solvents more rapidly. For example, the mesoporous PDA could finish the chromatism to methanol in minutes but the solid PDA required hours.

To improve the thermochromatic reversibility of PDA materials to higher temperatures, we designed amphiphilic precursors of diacetylene based on peptide.<sup>[23]</sup> The producing PDA materials consisted of two segments: the peptide segment and the alkyl chains, which were attached to the backbones. The peptide segments were stable upon heating due to the multiple hydrogen-bonding interactions. However, the backbone of PDA in alkyl chains experienced reversible conformational changes. In consequences, the reversible thermochromatic changes could happen at high temperature of 200 °C.

Although the above PDA materials show stable and reversible color changes, the fabrication of novel diacetylene derivatives is sometimes expensive and tedious. Thus, simple synthesis of PDA crystals with reversible color change is important. Therefore, inspired by the structure transition of diene crystals under heating, we firstly synthesized metastable PDA crystals *via* reacting NaOH with a diacetylenic acid in aqueous solution.<sup>[24]</sup> The synthesized PDA crystal had strong intermolecular interactions among side chains, which resulted in increases of molecular and bond angle constraints. As shown in Figure 1a, the irreversible chromatism from red to blue would happen when heating at 55–65 °C because the internal strain of the metastable PDA would be released, following the increases of effective PDA conjugation length. Nevertheless, the stable PDA crystals with a reversible thermochromatism of blue-to-red at a temperature range of 70–95 °C were produced from the metastable PDA crystal by the electrostatic interaction. However, with the temperature increase to over 130

°C, the irreversible chromatism from red to orange would happen due to the disordering of the PDA backbones.

## 2.2. Chromatic materials responding to new external stimuli

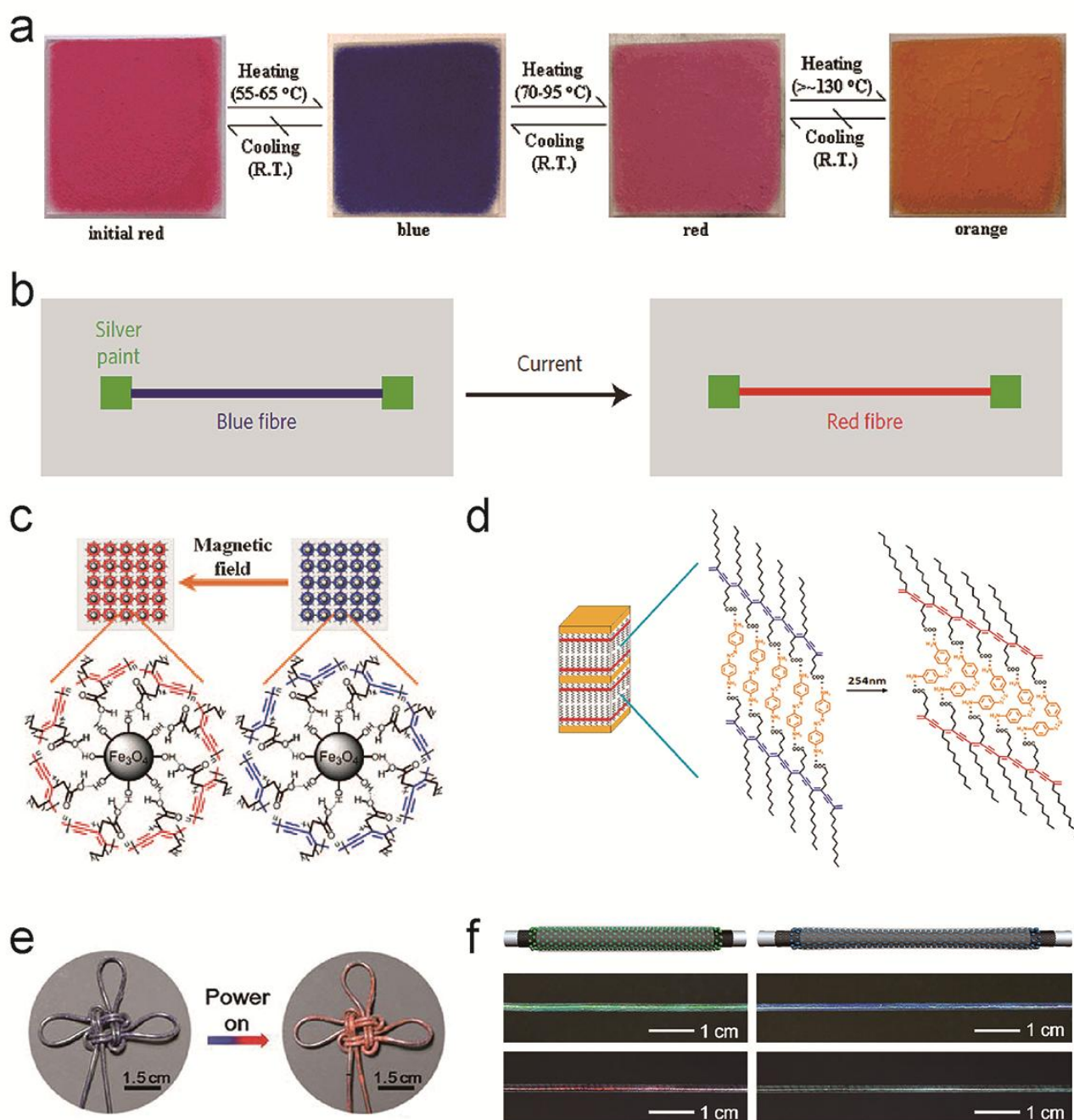
Although thermochromatic reversibility of PDA has been greatly improved, PDA can only respond to limited environmental stimuli, including heating, chemicals and pH.<sup>[10]</sup> To broaden the application of PDA materials, we invented some novel PDA composites which can respond to current, magnetic field and UV light.

Current-induced chromatism had never been reported probably because of the low conductivity of PDA. However, corresponding materials are very promising in the evaluation and detection from small facilities to aircrafts. Reminding by the reversible thermochromatism, it will be possible and convenient to achieve the electrochromatism by forming nanocomposites. Thus, a composite fiber was synthesized by directly introducing aligned CNTs into diacetylenic precursors, followed by topochemical photopolymerization of diacetylenic moieties.<sup>[25]</sup> As shown in Figure 1b, the resulting composite fiber could change colors from blue to red when a current with a range of 10–30 mA passed through the fiber. More importantly, the electrochromatism was much faster (typically less than 2 s) than the other reversible chromatism induced by heating or pH. The current-induced chromatism was summarized more probably from interactions between PDA and CNTs. Thus, when current passes, PDA/nanotube composite fibers produce electric fields between neighboring CNTs. Therefore, polar side chains of PDA are polarized, which results in the conformation distortion of PDA with color changes. Under low currents, the backbone of PDA can return to the original state upon removal of current. The electrochromatism is thus reversible. Nevertheless, high current may damage the recovery ability of the PDA conformation. It is also possible to achieve electrochromatism of PDA through introducing other conducting nanomaterials such as metal nanowires and conductive polymers.

Although the electrochromatism has been realized in PDA/CNT composites, the stability and current range may be further enhanced for more practical applications. To this end, novel electrochromatic materials consisting of polyacetylene derivative (poly[1-phenyl-2-(p-trimethylsilyl) phenylacetylene]) (PTP) and aligned CNTs were reported.<sup>[26]</sup> The composites demonstrated fast changes in both fluorescent intensity and color appearance responding to currents from 20 to 240 mA. Besides, the electrochromatism was reversible over a thousand cycles. The color change of above composites was caused by the conformation transition of polyacetylene derivative when currents passed. The above mechanism can be explained in two aspects. Firstly, there exist  $\pi$ - $\pi$  interactions between the benzene rings in polymer side chains and CNTs, which is sensitive to electric fields. Secondly, CNTs can be heated when passed with currents, which will induce color and fluorescent variation of PTP. Thus, the electric energy could be transferred to the PTP *via* aligned CNTs due to the  $\pi$ - $\pi$  interactions and simple heating, which could be increased by enhancing the currents or transfer efficiency.

In addition to electric current, magnetic field can also be readily, accurately and safely performed. However, magnetism-induced chromatism had never been realized in PDA. Consequently, inspired by the above fabrication of electrochromatic composites, we had incorporated Fe<sub>3</sub>O<sub>4</sub> nanoparticles into PDA. The resulting PDA composites exhibited chromatism from blue to red in magnetic field (Figure 1c).<sup>[27]</sup> The reason for above phenomena is that superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles produced heat internally and locally through Néel relaxation under magnetic field. The produced heat may induce the conformation change of surrounding PDA, which can be reflected by the color change.

Few studies were reported on light-induced chromatism in PDA. To compensate for the limitation, we introduced azobenzene moieties into PDA to fabricate nanocomposites with light-



**Figure 1** (a) Photographs of chromatic PDA composites at different temperatures. Reproduced with permission from ref. 24, copyright 2006 American Chemical Society. (b) Schematic illustration of electrochromatic PDA/CNT fiber when current passed through it. Reproduced with permission from ref. 25, copyright 2009 Nature Publishing Group. (c) Schematic illustration of the magneto-chromatic PDA/Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Reproduced with permission from ref. 27, copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Schematic illustration of conformation changes of photochromic PDA/azobenzene composites under UV irradiation. Reproduced with permission from ref. 28, copyright 2010 American Chemical Society. (e) Photographs of Chinese knot made of flexible and stretchable fiber of electrothermal chromatism. Reproduced with permission from ref. 11, copyright 2016 The Royal Society of Chemistry. (f) Schematic illustration and photographs of mechano-chromic fiber before and after stretching. Reproduced with permission from ref. 12, copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

induced chromatic properties.<sup>[28]</sup> As shown in Figure 1d, alternated lamellar mesostructure was formed with assembly of PDA and azobenzene. The above nanocomposites could transit from blue to red colors under UV irradiation, as the conformation of PDA changed due to isomerization of azobenzene from *trans* to *cis*. The lengths of PDA side chains were critical for transfer effi-

ciencies of the conformation transition from azobenzene to PDA, which could influence the speed of the chromatism. The shorter the side chains are, the faster the transition occurs. Unfortunately, the UV-induced color change was irreversible, specifically, the red could not revert to blue when azobenzene transits back *trans* from *cis*.

### 2.3. Increasing flexibility and number of chromatic colors

Great improvements have been achieved in PDA materials from higher reversibility to responsiveness to more stimuli. Nevertheless, the most PDA materials occur as powders or films with limited colors (mainly blue and red), which cannot meet the requirements for wearable electronics that is a mainstream in the future. Consequently, many efforts are needed to be devoted to increasing the softness and colors of chromatic materials.

PDA materials generally show poor mechanical properties because of their low structural regularity. Therefore, by introducing peptide-based amphiphiles into PDA monomers, we fabricated continuous thermochromic PDA fibers by topochemical photopolymerization under UV irradiation.<sup>[23]</sup> The produced fibers were strong and demonstrated ultrafast and reversible thermochromism.

To increase the flexibility and stretchability further, a PDA/CNT/polydimethylsiloxane (PDMS) fiber was developed using an elastic PDMS fiber substrate wound with aligned CNTs.<sup>[11]</sup> As shown in Figure 1e, the resulting fiber showed rapid electrothermal chromaticism, where the conductivity is mostly contributed from the aligned CNTs. Additionally, the reversible color change was well sustained during and after twisting and bending over 1000 cycles. The high reversibility and stability are due to the multiple hydrogen bonds offered by peptide segments in the side chains of PDA.

Although chromatic PDA/CNT composite fiber exhibited outstanding optical and mechanical properties, their displayed colors were limited to mainly red and blue. To offer more colors, a mechanochromic photonic crystal fiber was fabricated *via* electrophoretic deposition of polystyrene microspheres on the aligned CNTs, which had been wound onto a PDMS fiber, followed by embedding in PDMS.<sup>[12]</sup> The color of the mechanochromic fibers could be controlled through sizes of and distances among the polystyrene microspheres. As shown in Figure 1f, this mechanochromic fiber demonstrated rapid color changes among green, blue and red during stretching and releasing with both high sensitivity and reversibility. The high stability was maintained after over 1000 deformation cycles.

To meet the requirements of large-scale manufacture of chromatic fibers due to the need of commercially smart textiles, a novel method was adopted to continuously produce elastic mechanochromic fibers *via* dip-coating microspheres on commercial black spandex fibers.<sup>[29]</sup> The microsphere consisted of a soft poly(ethyl acrylate) shell and a hard polystyrene/poly(methyl methacrylate) core. Photonic crystals assembled from the microspheres displayed structural colors. The color of the fiber could be controlled by changing the diameters of microspheres. This strategy is applicable and efficient for a series of fibers with various diameters and cross-sections. The mechanochromic fibers demonstrate clear, rapid and reversible color changes such as red-green and green-blue under stretching. They can be woven into designed fabrics with potential applications in smart textiles.

In addition, several novel chromatic textiles were developed as well to meet the requirement of smart wearable textiles. For instance, a new flexible and stretchable strip thermochromic resistive heater was developed by introducing aligned CNTs to thermochromic silicone elastomer.<sup>[30]</sup> Besides, a smart chromatic fabric was developed by a low-cost and simple approach based on a single-sided conductive polyester-covered cotton fabric with light color.<sup>[31]</sup> The conductive cotton substrate was fabricated through selective deposition of polypyrrole. The highly conductive polypyrrole coating offered the fabric excellent resistive heating capabilities.

## 3. Deformation

Deformation is another representative responsiveness. De-

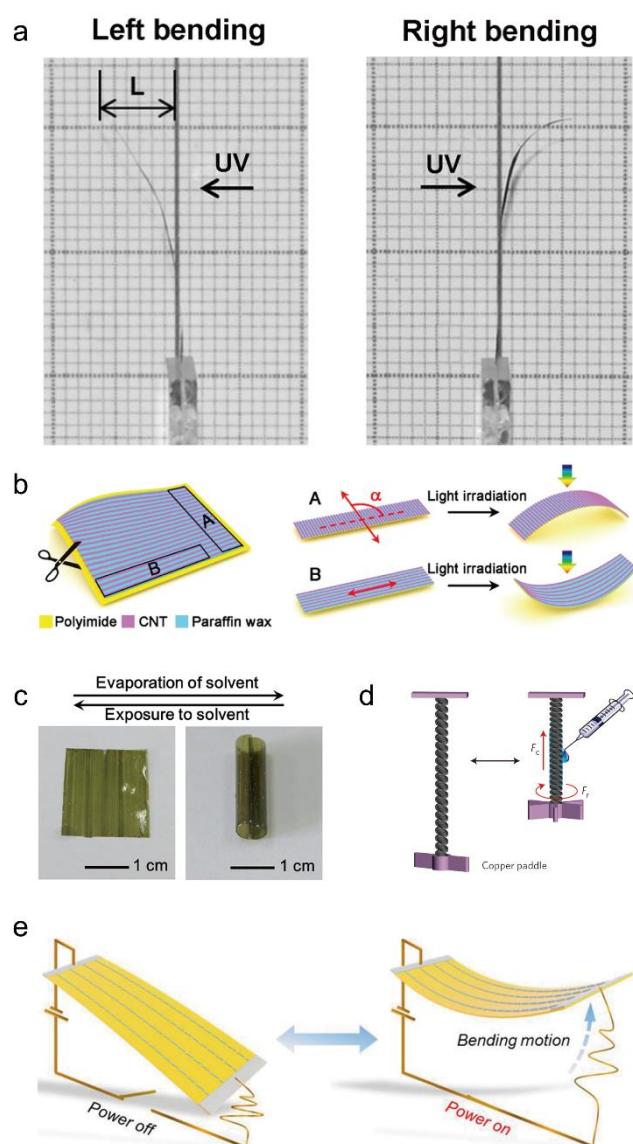
formation materials have attracted a lot of attentions in many fields such as micromachines, sensors and artificial muscles.<sup>[15,32-33]</sup> However, there remain lots of challenges to be solved for their practical applications.

Photodeformable materials have been investigated deeply. Among them, photoresponsive liquid-crystalline polymers are really attractive. ALCPs could deform reversibly under the irradiations of alternate UV and visible light, as the conformation of azobenzene changed between *trans* and *cis*.<sup>[34]</sup> Generally, ALCPs show irreversible deformation under the same light. However, it is not allowed or available to switch two different lights in some conditions. To overcome this limitation, we incorporated aligned CNTs into ALCPs. As shown in Figure 2a, the resulting nanocomposites demonstrated a reversible photodeformation under the UV light alone. The stress of the photodeformation is nearly 260 times higher than that of the strongest skeletal muscle. When UV was irradiated on one side of above composite strip, the conformation of azobenzene transitioned from *trans* to *cis* while the azobenzene moieties of the opposite side remained unchanged, which resulted in strip bending away from the light source. There are strong interactions between the CNT and azobenzene units. Therefore, under the reverse irradiation direction, the composite strip would bend away from the UV again. As a result, the reversible deformation could be repeated by hundreds of cycles with both high stability and sensitivity.

However, it is hard to accurately and rapidly control the deformation direction. To tackle this bottleneck, we came up with a bionic strategy for making visible light-responsive actuators with tunable and diverse deformations by combining aligned CNTs with paraffin wax on polyimide membrane.<sup>[35]</sup> The CNTs resemble the cellulose fibrils of plants, and the paraffin wax functions as the soft tissues. As shown in Figure 2b, photodeformation from phototropic to apheliotropic actuations was realized by controlling the CNT-aligned direction. The aligned CNTs were anisotropic materials with a low transverse modulus but a high longitudinal modulus, which constrained the expansion of paraffin wax. Therefore, the paraffin wax preferred to broaden the spaces among CNT bundles in transverse direction upon heating, resulting in the tensile stress. In addition, due to the different thermal diffusion rates among environment and the strip, the temperatures in the middle were higher than those at the edges after illumination. Therefore, the middle area of the strips extended more than the edges, producing a contractile stress in the longitudinal direction. The tensile and contractile stresses would compete with each other during the illumination. Here, the polyimide substrate resisted shearing deformation, so the deformation of the strips maintained the Gaussian curvature. Thus, the photo-thermal deformation could be programmed by tuning the structure of the strips. Besides geometrical constraint, the CNTs can also absorb visible and infrared light, which made the resultant actuators respond rapidly.

Besides photodeformation, the same strategy could also be used to tune the deforming direction of solvent-responsive polymers. For example, we combined aligned CNTs with PTP to produce composites, which could undergo reversibly anisotropic bending/unbending deformations driven by solvents (Figure 2c).<sup>[16]</sup> The deforming direction could be precisely controlled to be perpendicular to direction of the CNT length, as the backbones of the conjugated polymers were induced to orient in the longitudinal direction of CNTs. Therefore, the solvent molecules could widen the space between the backbones along the transverse direction of the aligned CNTs. In addition, the reversible deformation could repeat for 300 cycles with a stress of 15 MPa thanks to the strong  $\pi$ - $\pi$  interactions between CNTs and PTP.

To further improve the stability and adaptability to different media, we developed fiber actuators with pure aligned CNTs because of their outstanding properties. For example, fiber actuators



**Figure 2** (a) Photographs of an CNT/ALCP composite strip during the reversible deformation under the same UV light. Reproduced with permission from ref. 34, copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Schematic illustration of polyimide/CNT/paraffin wax strips with same aspect ratio but different CNT orientations showing apheliotropic and photomechanical deformation. Reproduced with permission from ref. 35, copyright 2015 American Chemical Society. (c) Images of a PTP/CNT composite film deformed upon absorption and evaporation of ethanol. Reproduced with permission from ref. 16, copyright 2014 The Royal Society of Chemistry. (d) Schematic illustration of the rotary and contractive actuations of a helical CNT fiber. Reproduced with permission from ref. 36, copyright 2015 Nature Publishing Group. (e) Schematic illustration of electromechanical bending generated by a ribbon woven from spring-like fibers. Reproduced with permission from ref. 38, copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

of hierarchically helical structure were presented here, which could respond to solvents and vapors reversibly and fast (Figure 2d).<sup>[36]</sup> The helical actuators were formed by twisting primary fibers composed of helical assemblies of aligned CNTs. The special structure of micrometer-scale gaps between the primary fibers and the nanoscale gaps among the CNTs contributes to large actuation stroke and fast response. Besides, the compact coils of the above fibers resulted in the reversible rotation. However, the above aligned CNT fibers could not respond to water because

they are hydrophobic. Whereas, water- or moisture-induced actuation is critical for a lot of applications. To overcome this problem, we prepared a hierarchically helical and hydrophilic CNT fiber by twisting hydrophilic primary fibers.<sup>[37]</sup> The hydrophilic primary fibers were fabricated by treating primary CNT fibers with oxygen plasma. The resulting fiber actuators could respond fast to water and had high rotation outputs and large contractive strokes. In addition, the above two kinds of fiber actuators were also strong, flexible and lightweight, which were suitable for sensing applications or wearable electronics.

Although solvent-induced deformation is really important, the actuation response to electric current will be more convenient and processable. Consequently, a novel twisted CNT fiber actuator was proposed with reversible rotation, contraction and self-twisting when direct current passed through it.<sup>[17]</sup> The rotation angle and contraction strain exceeded 360° and 2%, respectively. The torsional rotation and longitudinal contraction were due to electromagnetic effects among helically aligned CNTs according to Ampere's Law. The microstructure in CNT fibers was important in improving the behaviors and performances of the actuators. Furthermore, coiled structures formed *via* an over-twisting process could enhance both rotation outputs and contractive strains triggered by electricity. To explore their practical applications, fabric ribbon actuators were fabricated by weaving coiled fibers into polymer films.<sup>[38]</sup> As shown in Figure 2e, the resulting ribbon actuator could bend programmatically. In addition, more sophisticated motions could also be controlled by weaving the helical CNT fibers into different forms such as artificial wings and tails.<sup>[39]</sup>

## 4. Integration

Although chromatism and deformation have been studied broadly, the single function may not satisfy some special practical applications. Therefore, it will be future trend to integrate smart materials with other devices such as supercapacitors and solar cells.

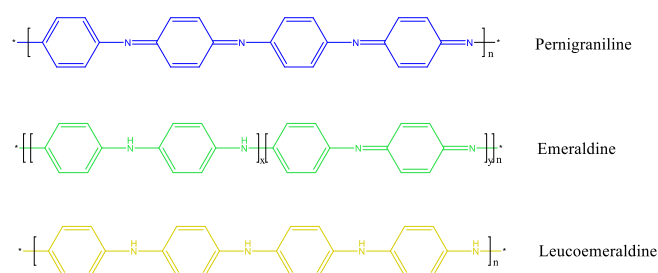
### 4.1. Chromatism integration

Electrochemical capacitors have been extensively investigated for energy storage thanks to their high-power densities.<sup>[40]</sup> During the daily life, we have to confront a difficulty of quickly knowing how much the energy left before our devices stop working. Thus, it is really important to achieve dynamic communications. Combining with the discussion in chromatism of conjugated polymers, it will be convenient to combine the energy devices with chromatic polymers.

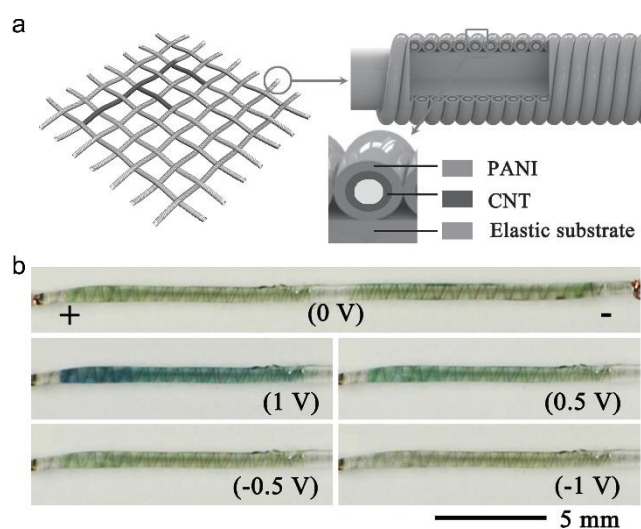
Therefore, we developed responsive supercapacitors by incorporating polyaniline (PANI) with aligned CNT electrodes paved on elastic PDMS substrate.<sup>[41]</sup> The supercapacitors showed rapid and reversible color changes among blue, green and yellow according to the working state, which could be observed by naked eyes. Thanks to the continuous, flexible and stretchable structure, the chromatic supercapacitor could maintain a specific capacitance of 308.4 F/g well after bending for 1000 cycles or stretching by 100% for 200 cycles. Here, as shown in Scheme 2, PANI mainly exhibited three structures, a fully reduced state called leucoemeraldine, a fully oxidized state called pernigraniline and emeraldine that falls in between leucoemeraldine and pernigraniline. At 1 V, PANI was blue at a form of pernigraniline; at 0.5 V, it was the protonated emeraldine with a green color; at 0 V, it was in a partly oxidized state with light green; at -0.5 V and -1 V, it was leucoemeraldine with a yellow color.

To meet the wearable requirements, a novel electrochromatic fiber supercapacitor was fabricated by electro-depositing PANI on the aligned CNT sheets wound onto a stretched PDMS fiber.<sup>[42]</sup>

**Scheme 2** Three molecular structures of PANI. Here  $n$  indicates the number of the repeating format, while  $x$  and  $y$  represent the percentage of each unit. Reproduced with permission from ref. 41, copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



The resulting fiber supercapacitor can be woven into fabrics further (Figure 3a). As shown in Figure 3b, this fiber supercapacitor showed a rapid and reversible color change similar to the above electrochromatic film capacitor based on the same mechanism. However, the other colors could also be achieved by choosing other organic or inorganic materials according to the same method. The above electrochromatic fiber capacitors also demonstrated great electrochemical performances under different deformations such as stretching and bending. Besides energy storage, the same strategy can also be adopted for the other devices such as displays and sensors.



**Figure 3** (a) Schematic illustration of the fabric and structure of the electrochromatic fiber supercapacitor. (b) Photographs of an electrochromatic fiber supercapacitor and the positive electrode during the charge-discharge process. Reproduced with permission from ref. 42, copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

#### 4.2. Deformation integration

Remotely tunable photoelectric conversion is hard to realize in solar cells, which may be adverse for practical applications such as microelectronics. Therefore, we presented a fiber photoelectric conversion device *via* the integration of photomechanical actuation and the electrostatic effects.<sup>[43]</sup> The fiber photoelectric conversion device consisted of two functional electrodes. One electrode was a composite of aligned CNT fiber and poly(tetrafluoroethylene) with the function of charge storage, while the other included a strip of polyimide that was coated with aligned CNT/paraffin wax for photomechanical actuation. As shown in Figure 4a, the distance among the two electrodes changed periodically because of the repeated bending and releasing of the

novel photoelectric devices under the regular irradiation of visible light. The above process produced potential differences due to the changes of the number of induced charges. Besides, the fiber device showed controllable output voltages with both high flexibility and stability, endowing them potentials in wearable electronics.

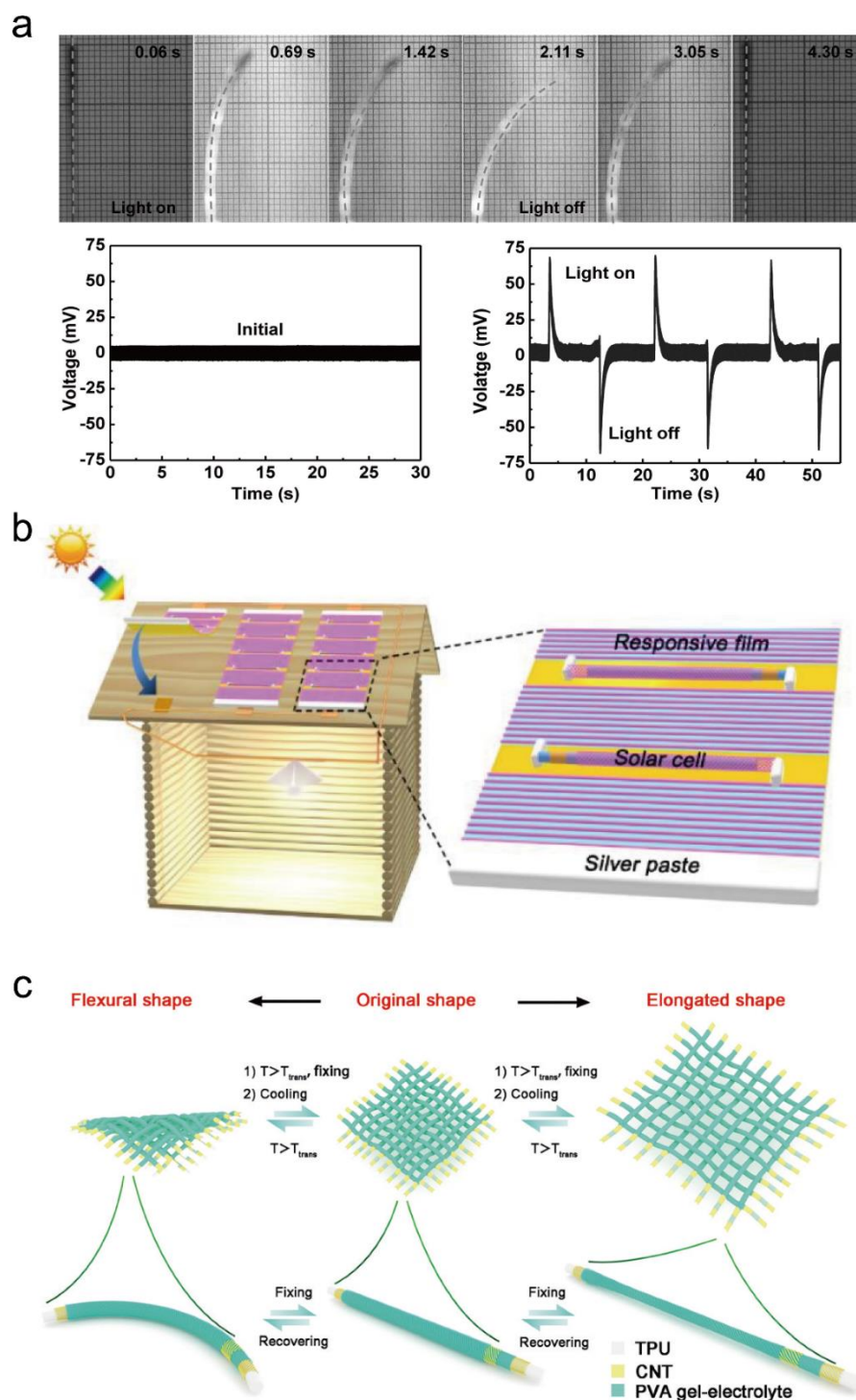
However, the above device generated pulse potential, which is adverse for actual use. In consequence, we integrated a photo-induced actuator with fiber perovskite solar cells to develop a solar energy-harvesting system.<sup>[35]</sup> The photo-responsive actuations of the actuator were slightly affected because the fiber solar cells were small and lightweight. As shown in Figure 4b, the above system was installed on a cabin roof. The system would open automatically when the sunlight lamped the roof. As a result, the solar cells began to work to power the light emitting diodes. The above smart system is potential in some fields such as intelligent electronics and mechanical engineering.

Besides the energy-harvesting, energy storage is also critical. Adaptable energy storage systems are highly required while unavailable to power the wearable electronics. Thus, a shape-memory fiber supercapacitor was fabricated by winding aligned CNTs onto a shape-memory polyurethane substrate.<sup>[44]</sup> As shown in Figure 4c, the fiber supercapacitor could deform and be “frozen” as expected; it could recover automatically to the original size and shape when required. Its electrochemical performances were kept up well when it was deformed, “frozen” and recovered to the original shape.

#### 5. Conclusions and Outlook

The realization of responsive polymer composite fiber can supplement the smart wearable electronics, which depicts a great blueprint to achieve the goal of smart textiles. Although remarkable achievements have been realized, there still remain grand challenges to meet the requirements for practical applications of responsive fibers. Given that numerous researches have endeavored to enhance the responsive reversibility, stability and controllability, more efforts should be devoted to improving the adaptability and functional integration. From the research progress summarized above, one can identify that incorporating less responsive or passive components into responsive subjects holds the key to dramatically enhancing the responsiveness of the resulting composites. Moreover, the aligned assembly of nanomaterials such as CNTs can endow themselves great responsive properties. Both the chromatic and deformational materials have been integrated with other functional devices including energy harvesting and storage, which have shown potentials in special applications.

The future studies to conquer the potential challenges in responsive fibers can be devoted to the following aspects. First, we can learn from biological organisms which can respond to the environmental stimuli, for example, chameleon that can change its color for camouflage and plants that can deform according to the water content in the environment. The second attempt is to integrate more functions into the responsive fibers because the resulting responsive system needs cooperations of different modules under different applicable conditions. For example, a smart communication system can display different colors or movements according to our emotional responses rather than using words, as we do not want to talk when we are upset or angry, especially for people with depression. The third aspect is manufacture of responsive fibers. As the above fibers have single or multiple functions, the corresponding facilities will be sophisticated. Therefore, the cooperation of different disciplines will be necessary. Besides, their biocompatibility, washability, endurance and photostability should meet the needs when they are adopted as wearable textiles.



**Figure 4** (a) Photographs and output voltages of the fiber photoelectric conversion device without and with the periodical visible light irradiation. Reproduced with permission from ref. 43, copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Schematic illustration of integration of a light-responsive actuator and several fiber perovskite solar cells on a cabin roof. Reproduced with permission from ref. 35, copyright 2015 American Chemical Society. (c) Schematic illustration of the shape-memory fiber supercapacitor and the produced textile which showed reversible deformation. Reproduced with permission from ref. 44, copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

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