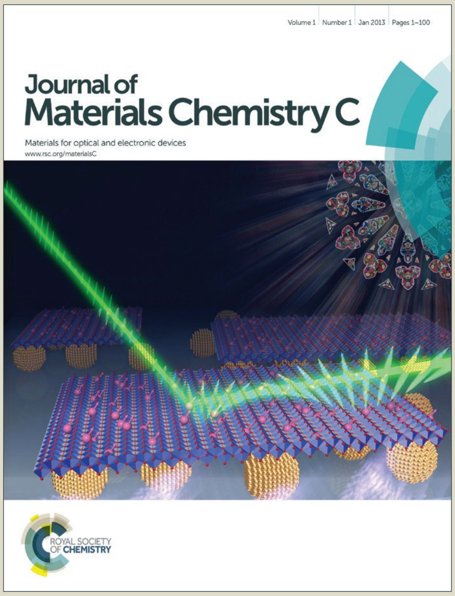
Journal of
Materials Chemistry C



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A continuous fabrication of mechanochromic fiber

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Abstract: A new strategy is demonstrated to continuously prepare dyeing-free mechanochromic fibers by dip-coating hard core-soft shell microspheres onto commercially available polymer fibers. The microspheres assemble into a photonic crystal structure to display structural colors, and the colors of these fibers can be easily controlled by varying the diameters of core-shell microspheres. The polymer fibers provide a high elasticity and stability to endure mechanical stretching. This method is efficient and applicable for a variety of fibers with different diameters and cross-sectional shapes and a broad spectrum of polymer and inorganic substrates. The mechanochromic fibers exhibit obvious color changes such as from red to green and from green to blue under stretching, and these chromatic transitions are rapid, reversible and repeatable. They are further woven into well designed patterns and fabrics for potential application in smart wearable textiles.

Our world is a riot of colors, some of which are chemical colors resulting from the pigments which give substances colors by absorbing lights at specific wavelengths, and some of them are structural colors originating from the Bragg scattering of microstructures in materials, which widely exist in plants and animals.[1-5] A lot of efforts have been devoted to developing artificial structural colored materials, because the structural coloration is free of dye, brilliant, unfading, and in consistence with requirements of sustainable development.[6-9] Among them, three-dimensional photonic crystal material from the self-assembly of colloidal microspheres represents one of the most attractive materials for structural colors. In addition, the structural colors based on the photonic crystal structure are changeable by varying the distance of two neighboring lattice planes or the refractive index contrast between two media.

To this end, various responsive structural colored materials had been developed in response to the surrounding environmental stimuli, including mechanical deformation[10, 11], temperature changes[12], magnetic fields[13], electric fields[14], solvent or vapor infiltration[15, 16], pH changes[17] and special molecular[18]. They are promising for the applications in various areas such as smart displays[15, 19] and sensors[11, 20, 21], especially in textiles.[22-24] Among them, mechanical deformation represents a straightforward and effective way to change the structural color compared with the slow response to solvent, heat and light and the inconvenience of electric or magnetic fields.

A lot of mechanochromic films with structural colors have been widely explored based on the crosslinking process of core-shell microspheres, infiltration elastomer into assembled hard microspheres, and non-close-packed colloidal and inverse opal structure.[10, 25-27] However, mechanochromic materials in a fiber shape have not appeared until recently possibly due to the difficulty to directly arrange the microspheres into fibers or orderly coated on the curved surface of fiber substrate by time consuming gravitational sedimentation or vertical deposition process.[28] On the other hand, making structural colored materials into a fiber shape may represent a promising strategy for environment-friendly textile industry, as the fiber is the basic material. Previously, mechanochromic photonic crystal fibers were successfully fabricated by the infiltration of elastic polymers into electrophoretically deposited colloidal microspheres and extrusion process of core-shell microspheres.[22, 29] However, the requirement of elastic conductive fiber substrate for electrophoretic deposition, and the high temperature and poor mechanical properties from the extrusion process hamper the generalization of these methods. It is urgently needed but remained challenging to develop effective methods that are compatible with the typical textile technologies in synthesizing chromic fibers.

Herein, a general and efficient strategy is demonstrated to continuously prepare a new family of dyeing-free mechanochromic fibers (MCFs) by coating hard core-soft shell microspheres onto commercially available black spandex fibers. The microspheres assemble into a photonic crystal structure to display brilliant colors covering the visible light region, and the colors of these fibers can be easily controlled by varying the diameters of core-shell microspheres. The polymer fibers provide a high elasticity and stability to endure mechanical stretching. This method is applicable for a variety of fiber shapes such as circle, rectangle and triangle and a broad spectrum of substrates including polymers and inorganic materials. The MCFs also exhibit obvious color changes such as from red to green and from green to blue under stretching, and these chromatic transitions are rapid, reversible and repeatable. They are further woven into well designed and complex patterns for potential application in textile industry, which is particularly promising for the next-generation wearable applications.

The preparation of the MCF is displayed in **Scheme 1** and detailed in the Supporting Information. Briefly, core-shell microspheres with a hard polystyrene/poly(methyl methacrylate) (PS/PMMA) core and a soft poly(ethyl acrylate) (PEA) shell are first synthesized by semi-continuous and stepwise emulsion polymerization.[25] The as-fabricated core-shell microsphere latex is further concentrated to a high solid content in water by the evaporation of water. Commercial black spandex fibers are then treated by oxygen plasma to increase the hydrophily and serve as substrates. The core-shell microspheres are finally coated onto the spandex fibers through a continuous solution based on the design of two electric motors (**Figure S1**). It is worth noting that, the utilization of hard core-soft shell microspheres, the concentration of microsphere dispersions and modification of spandex fibers are very critical for the fabrication of MFCs, which will be discussed later.

Figures 1a-c show transmission electron microscope (TEM) images of PS cores, PS/PMMA microspheres and PS/PMMA/PEA core-shell microspheres, respectively. Along with the coating of PMMA interlayer and PEA shell, the diameters of microspheres were increased gradually from 184 nm (PS) to 206 nm (PS/PMMA) and then to 273 nm (PS/PMMA/PEA). The diameters could be tuned by changing the synthetic parameters such as the content of emulsifier, and they are summarized at **Table S1**. All microspheres showed a PS/PMMA hard core and a PEA soft shell typically with a diameter ratio of 3/4 between the core and the whole microsphere. In addition, the diameters of all the microspheres were uniform with particle dispersion indices below 0.04 based on dynamic light scattering measurements. The core-shell microsphere dispersions were concentrated with high solid contents prior to use, and the concentrated dispersions were quite viscous while remained stable without obvious coagulation after 4 months at ambient temperatures (**Figure S2**).

The spandex fiber is a commercially available elastic fiber and has been widely used in textile industry. It is typically smooth and hydrophobic with a contact angle of 110° (**Figure S3**). In order to increase the affinity to the aqueous microsphere dispersion, the fiber was modified to be rough and hydrophilic with a contact angle of 70° by oxygen plasma treatment (**Figure S3**). The mechanical property of spandex fiber such as tensile stress had been well maintained after the oxygen plasma treatment (**Figure S4**). The microspheres can be coated on the fiber surface by a dip-coating process under ambient conditions without strict requirements compared with the other methods such as electrophoretic deposition. Additionally, the spandex fiber which was black could act as a good background for more saturated colors.[30]

The resulting core-shell microsphere layers were uniform on the elastic fiber (**Figures 1d** and **1e**), and they showed a thickness of tens of micrometers which is thick enough to show structural colors.[31] Due to the unique hard core-soft shell structure, the coated microspheres self-assembled into a close-packed photonic crystal structure and were connected with each other (**Figure 1f**). The strong connection among the soft PEA shells allowed microspheres to arrange effectively without obvious structure damage compared with the hard PS microspheres (**Figure S5**). It should be noted that, hexagonally arranged microspheres could be obtained on a planar glass substrate (**Figure S6**), while the arrangement of the coated microspheres on the surface of MCFs was not perfect at a large area although the microspheres are monodispersed, possibly due to the curved surface of the fiber. Although they formed ordered structure in numerous local areas, the coated layer was continuous and the fibers displayed brilliant structural colors.[32] It was also found that the concentration of microsphere dispersions and the hydrophily of the spandex fiber were important for the assembly of the microspheres into uniform layers on the fiber surface. For the microspheres with a diameter of 273 nm, a solid content of ~46% was typically used. When the as-obtained microsphere dispersion had a lower solid content of ~31 %, the microspheres were hardly coated onto the spandex fiber and the resulting fibers only showed colors in localized small areas (**Figure S7a**), possibly due to the low viscosity of the dispersion. Moreover, the coated microspheres could not effectively assemble into uniform layers on the spandex fiber without plasma treatment even by using a concentrated dispersion (**Figure S7b**).

Thanks to the commercially available spandex fiber (**Figure 2a**) and the efficient coating process, these MCFs could be continuously prepared. **Figures 2b** and **2c** show two rolls of green and blue fibers with a diameter of ~0.8 mm. The different colors were achieved by varying the diameters of the core-shell microspheres, which were controlled by the amount of emulsifier during the preparation of PS seeds. Herein, red, green and blue fibers were designed by choosing the core-shell microspheres with diameters of 216, 273 and 324 nm respectively. These MCFs shared a diameter of ~0.12 mm and they exhibited reflection peaks at 452, 555 and 650 nm, respectively (**Figures 2d-f**). The reflection peaks exhibited a linear relationship with the diameter of microspheres (**Figure S8**) in accordance with the Bragg's equation. However, due to the non-negligible incoherent scattering at short wavelengths, the red-colored fibers looked pale due to a lower color saturation.[33, 34]

Besides single spandex fibers, multi-ply spandex fibers can also be bundled as effective substrates to produce larger MCFs (**Figures 2g** and **2h**), and this property is compatible with the textile industry. Therefore, various diameters of the MCFs could be obtained by using multi-ply spandex fibers with different strands and single-ply spandex fibers with different diameters as substrates (**Figures 2g-i**). Interestingly, although the fibers from the same core-shell microspheres showed a similar reflection peak position (**Figure S9)**, the observed colors were different between the single-ply and multi-ply fibers. The multi-ply fibers exhibited colors with a stronger saturation possibly due to rougher surfaces (**Figure S10**). In addition, this method is applicable to a variety of fiber shapes, and circle, rectangle and triangle were studied as three demonstrations (**Figures 2j-l**). Note that this preparation method could be also extended to the other shapes such as thin films (**Figure 2m**) and textiles (**Figure 2n**) besides fibers, and it was also effective for various substrates such as glass (**Figure 2m**).

Benefiting from the unique core-shell structure and elastic substrates, the MCFs exhibited reversible color changes under deforming. For instance, the MCFs switched colors from red to green and from green to blue under stretching (**Figure S11**). This mechanochromic behavior was further characterized by optical microscopy and reflection spectroscopy. After being elongated from 0 to 50%, the MCF gradually changed colors from green to blue (**Figure 3a**), and the corresponding reflection peaks were gradually shifted from 554 to 495 nm (**Figures 3b** and **3c**). At the same time, the intensity decreased with increasing strains.

The main reflection position (λ) could be estimated by Bragg's equation of $\lambda=2d(n_{eff}^2-\sin^2\theta)^{1/2}$, where λ, d, n_{eff} and θ correspond to the reflection wavelength, the lattice spacing, the effective refractive index and the angle between the incident beam and the diffraction plane, respectively.[35] For mechanochromic colloidal crystals based on an elastomer, the change of d under strain is always accompanied by the change of the n_{eff}. However, the change of d causes a much more significant color shift than that of n_{eff}. Therefore, the effect of n_{eff} is not emphasized when the structural colors are tuned by varying d.[1, 36] The structural change of the elastic colloidal crystals under deformation had been addressed in the previous work mainly based on Poisson ratio and rearrangement of microspheres.[26, 37, 38] To summarize, when the MCFs were axially elongated under stretching, the soft PEA shell deformed, and the thickness of coated microsphere layer decreased in order to keep the total volume constant, which caused the decrease of the lattice spacing of photonic crystal structure in the radial direction. Meanwhile, the arrangement of hard PS/PMMA cores were changed from hexagons to squares with higher strains.[29] As a result, the reflection peaks displayed a blue shift with decreased intensities under stretching.[22, 26, 29, 37]

Meanwhile, as the MCF elongated, the applied force also gradually increased during the blue shift of the reflection spectra (**Figure S12**). When further stretched to a strain larger than 50%, the hard PS/PMMA cores were almost in contact with each other and the lattice constant in the radial direction of the fiber was no longer change, thus the reflection peak was invariable.[29] After releasing, they could recover back to the original arrangement and show obvious optical response.

The chromatic transitions were also reversible based on the reflection spectroscopy. The reflection peaks and intensities remained almost unchanged after stretching for over 2000 cycles (**Figures 3d** and **3e**). The high reversibility and repeatability were attributed to the unique structure of the MCFs with an elastic fiber in the core and chromic layer in the sheath. For comparison, chromic fibers consisted of only core-shell microspheres were also prepared by melt extruding process. The MCFs based on dip-coating process required less microspheres while with better mechanical properties than the melt-extruded fibers (**Figure S13**). For instance, after a drawing-and-releasing cycle with a strain up to 50%, the MCFs showed a residue strain of ~5%, and it took several seconds to return to the original state; in a strong contrast, the extrusion-based fibers retained about 25% strain after releasing, and several minutes were required for recovery. Additionally, these MCFs maintained high stability after deforming for 100 cycles, while the extrusion-based fiber showed poor cyclic property and broke off after tens of deformations. For practical application, the resistant to scrubbing was then tested by a standard laundry process in a washing machine. After washing, no significant structure damage was observed in MCFs (**Figure S14**). Moreover, the structural color and the corresponding reflection spectra were also maintained before and after washing (**Figure S15**), which demonstrated that the arrangement of microspheres was still ordered.

The one-dimensional configuration of the thin MCF provides unique advantages in many applications such as textiles and displays. They were lightweight (**Figure 4a**) and could be woven into a variety of textiles. For instance, they could be made into a hand chain (**Figure 4b**) and a fabric (**Figure 4c**) through the use of two colors of building fibers without any dyes or pigments. A more complex butterfly pattern had been also produced from three colors of building fibers (**Figure 4d**). In addition, the mechanochromic behaviors of the building fibers allowed the resulting textiles to change their colors under deforming. For instance, the hand chain that was made from red fibers at middle and green fibers outside (**Figure 4e**) switched the color of the middle fibers to green under stretching (**Figure 4f**).

In summary, a new continuous process by dip-coating hard core-soft shell microspheres onto elastic polymer fibers was developed to prepare MCFs with high performances. The microspheres assembled into a photonic crystal structure to display structural colors, and the colors of these fibers were controlled by varying the diameters of microspheres. The use of hard core-soft shell microspheres and their concentration played important roles in the MCF fabrication. This method is suitable for a variety of fibers with different diameters and cross-sectional shapes such as circle, rectangle and triangle and a broad spectrum of substrates including polymers and inorganic materials. These fibers also exhibited rapid and reversible color changes in the range of visible light under stretching and releasing cycles with high repeatability. They were further woven into textiles to show colorful and tunable patterns. This easy and green fabrication method provides a new platform for chromic fibers and textiles to possibly alternate the traditional dyeing technique and has promising applications in smart wearable textile industry.

Acknowledgements

This work was supported by NSFC (21225417, 51573027, 51403038), STCSM (12nm0503200, 15JC1490200), China Postdoctoral Science Foundation (2047M560290, 2015T80391), and the Program for Outstanding Young Scholars from Organization Department of the CPC Central Committee.

Keywords: structural color, mechanochromic, fiber, textile

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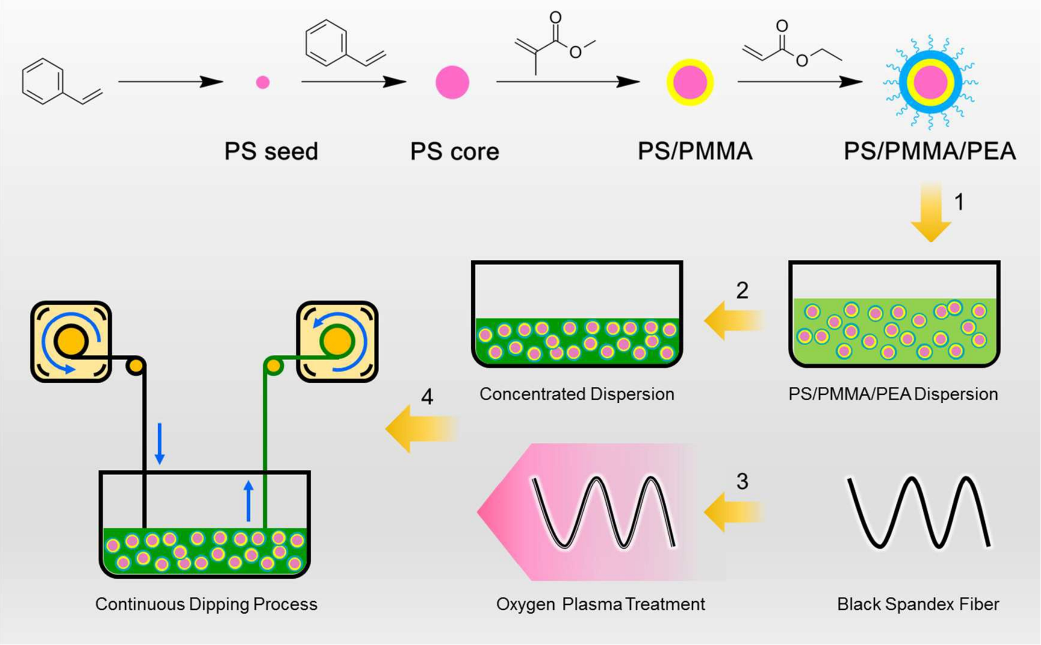

Scheme 1. Schematic illustration to continuous preparation of the mechanochromic fiber in four steps: 1) synthesis of core-shell microspheres; 2) concentration of microsphere dispersions; 3) surface modification of spandex fibers; and 4) continuous deposition of microspheres onto spandex fibers.

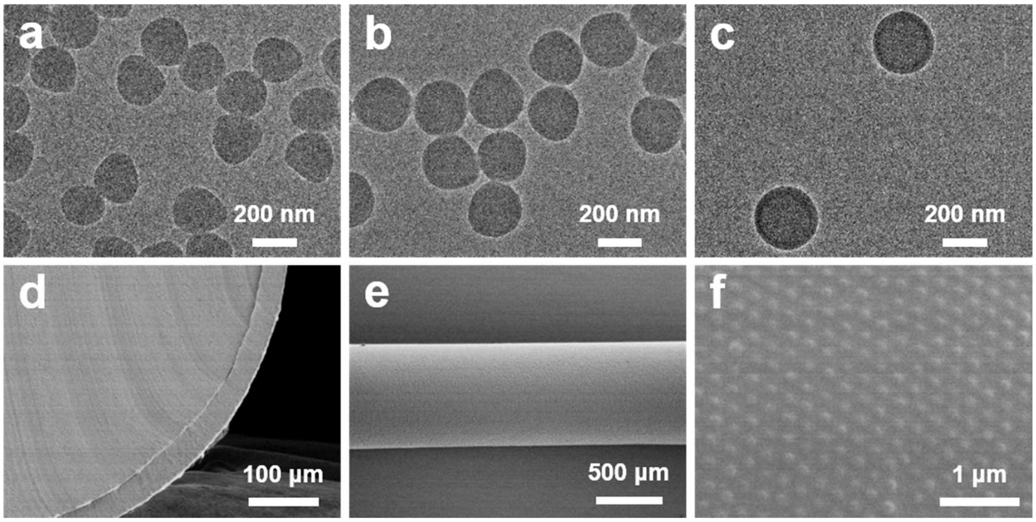

Figure 1. Structure characterization of core-shell microspheres and MCFs. (**a-c**) TEM images of PS microspheres, PS/PMMA microspheres and PS/PMMA/PEA microspheres, respectively. The diameters of all the microspheres were uniform with particle dispersion indices below 0.04. (**d**) and (**e**) SEM images of the MCF deposited with PS/PMMA/PEA core-shell microspheres (diameter of 273 nm) by cross-sectional and side views, respectively. (**f**) Higher magnification of (**e**).

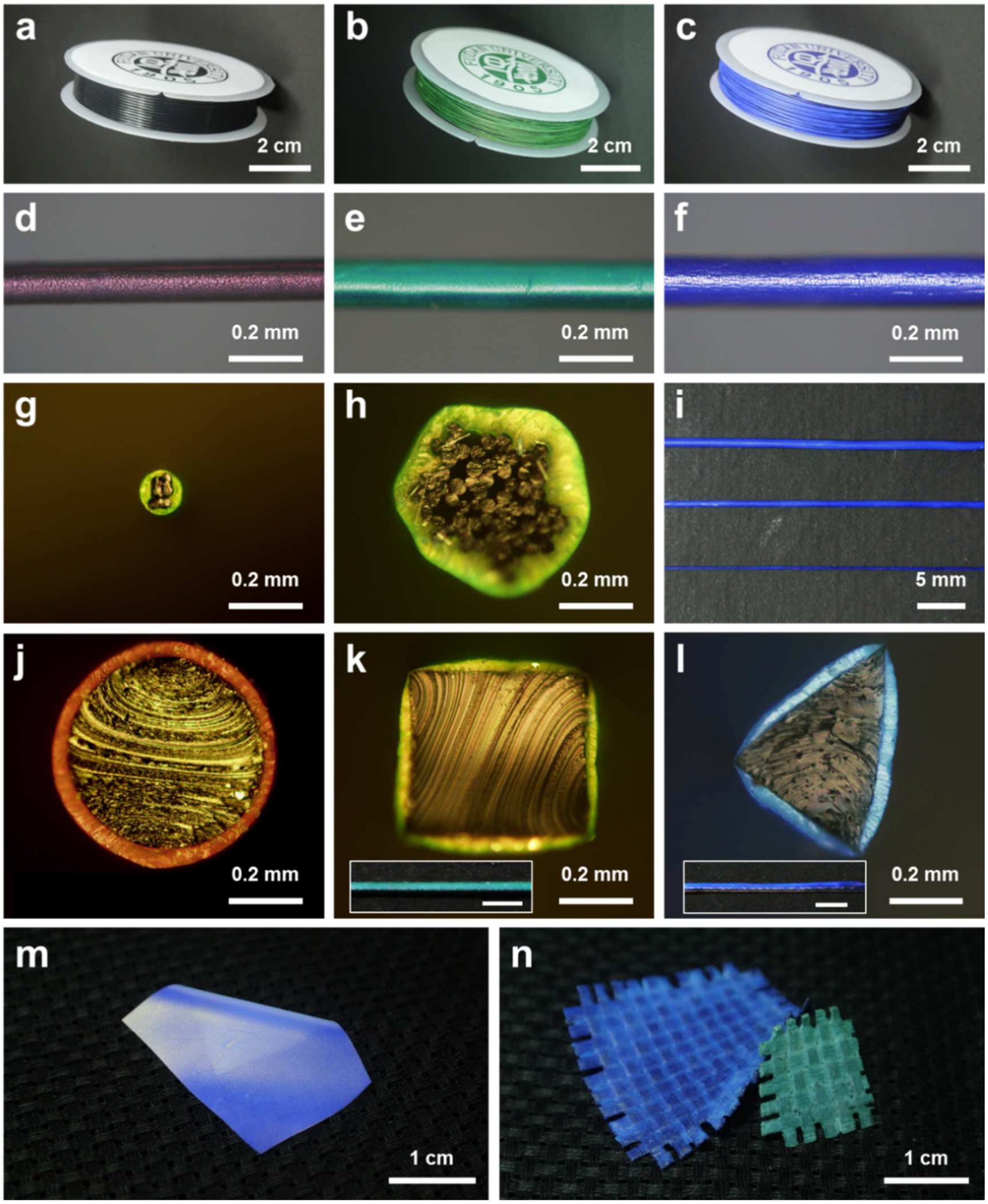

Figure 2. Preparation of different MCFs. (**a-c**) Photographs of a black spandex fiber and the resulting green and blue fibers in a roll, respectively. (**d-f**) Optical micrographs of red, green and blue fibers, respectively. (**g**) and (**h**) Cross-sectional optical micrographs of MCFs based on six-ply and sixty-ply spandex fibers, respectively. (**i**) Photographs of three blue fibers with different diameters. (**j-l**) Cross-sectional optical micrographs of MCFs with different shapes of circle, rectangle and triangle, respectively (inset, photographs of MCFs in side view, scale bar, 2 mm). (**m**) Photograph of a blue film. (**n**) Photograph of blue (left image) and green (right image) textiles.

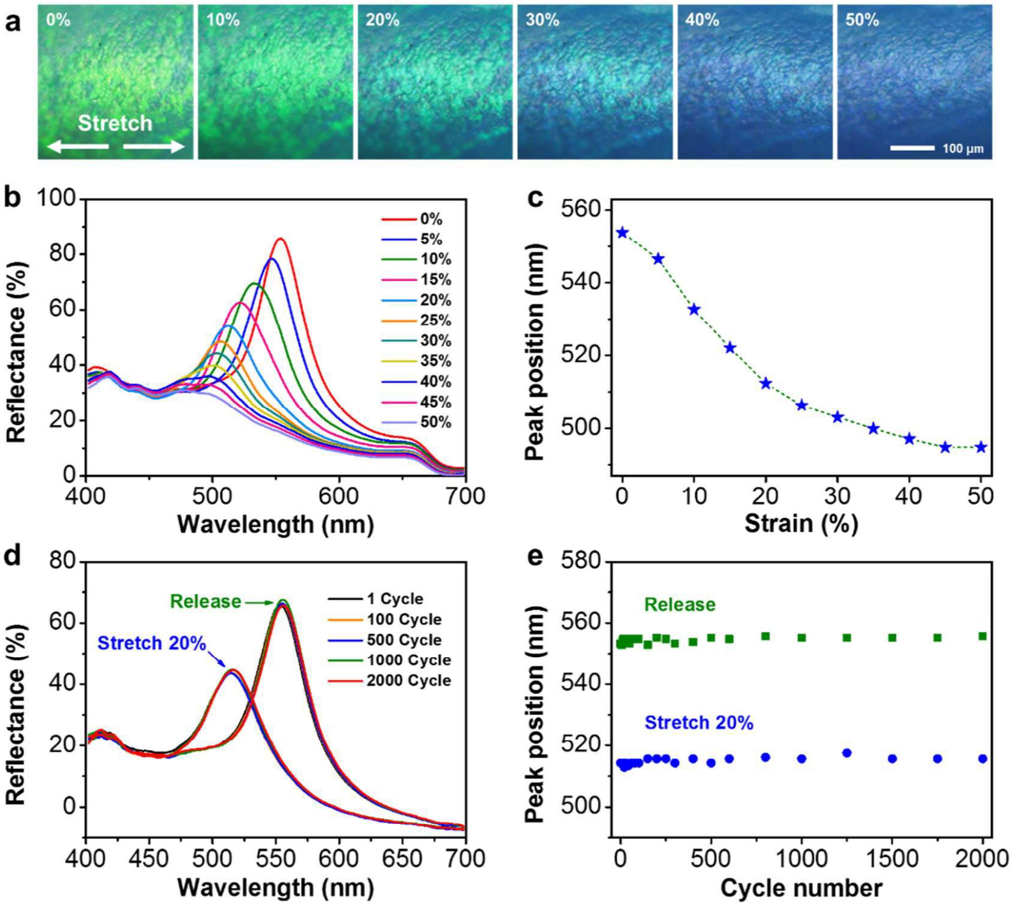

Figure 3. Mechanochromic performance of the composite fiber. (**a**) Optical micrographs of the fiber made from PS/PMMA/PEA core-shell microspheres with a diameter of 273 nm at increasing strains from 0 to 50% with colors being changed from green to blue. (**b**) Reflection spectra at increasing strains. (**c**) The variation of peak position with increasing strains at (**b**). (**d**) Reflection spectra after stretching (strain of 20%) in different cycles. (**e**) The evolution of peak position over 2000 cycles.

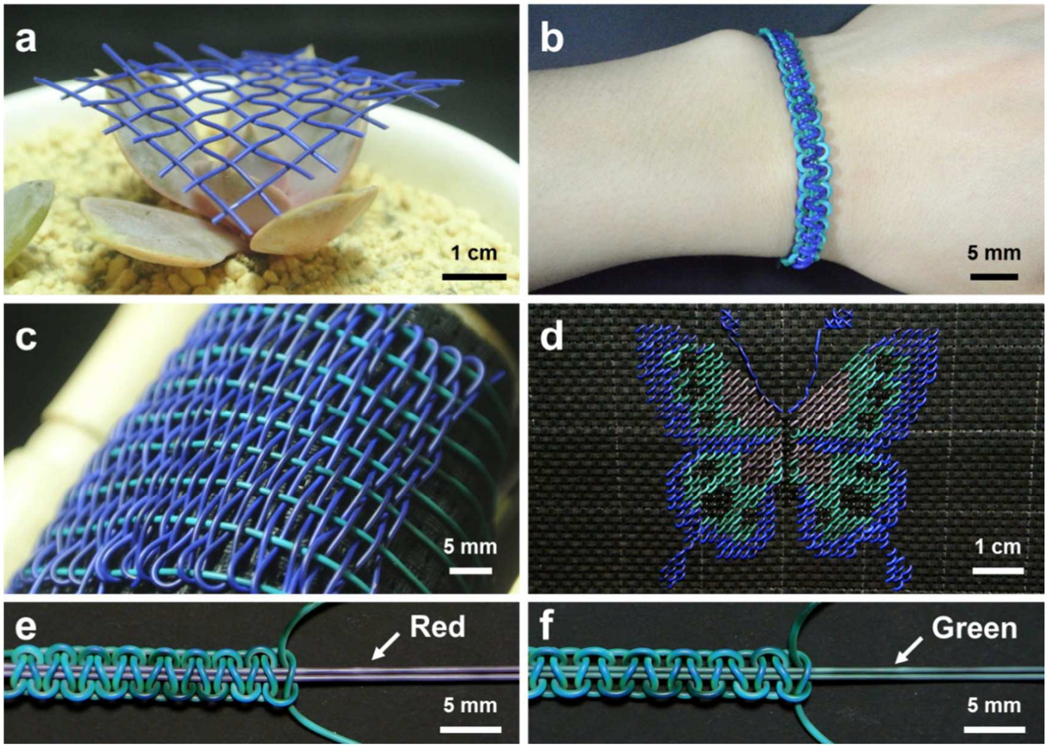

Figure 4. Photographs of chromatic patterns and textiles made from MCFs. (**a**) A fabric made from blue fibers with a diameter of ~0.5 mm. (**b**) A hand chain made from blue and green fibers. (**c**) A piece of textile made from blue and green fibers. (**d**) A colorful cross embroidery made from fibers with red, green and blue colors. (**e)** and (**f**) A mechanochromic hand chain before (**e**) and after (**f**) stretching with two middle fibers changing color from red to green.

Table of Contents

New mechanochromic fibers are continuously developed by coating concentrated core-shell microspheres onto elastic polymer fibers with low cost and high efficiency.