The continuous fabrication of mechanochromic fibers†

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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 exhibit 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 exist widely 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 the requirements of sustainable development.6–9 Among them, the three-dimensional photonic crystal material obtained 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 have 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 changes17 and special molecules.18 They are promising for applications in various areas such as smart displays15,19 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, fiber shaped mechanochromic materials had not appeared until recently possibly due to the difficulty in the direct arrangement of the microspheres into fibers or ordered coating on the curved surface of the fiber substrate using a time-consuming gravitational sedimentation or vertical deposition process.28 On the other hand, transforming structural colored fibers may represent a promising strategy for environment-friendly textile industries, 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 the extrusion process of core–shell microspheres.22,29 However, the requirement of elastic conductive fiber substrates 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 remains a challenge 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 mechanochromatic 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 exhibit
high elasticity and stability to endure mechanical stretching.
This method is applicable for a variety of fibrous 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 the textile industry, which is particularly promising
for next-generation wearable applications.

The preparation of the MCF is displayed in Scheme 1 and
detailed in the ESI.† 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
via semi-continuous and stepwise emulsion polymerization.25
The as-fabricated core–shell microsphere latex is further con-
centrated to a high solid content in water via the evaporation
of water. Commercial black spandex fibers are then treated under
oxygen plasma to increase the hydrophilicity 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 (Fig. S1, ESI†). It is worth noting
that the utilization of hard core–soft shell microspheres, the
concentration of microsphere dispersions and the modification
of spandex fibers are very critical for the fabrication of MFCs,
which will be discussed later.

Fig. 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
the PMMA interlayer and PEA shell, the diameters of the micro-
spheres 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 in Table S1
(ESI†). 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 measure-
ments. 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
(Fig. S2, ESI†).

The spandex fiber is a commercially available elastic fiber
and has been widely used in textiles. It is typically smooth and
hydrophobic with a contact angle of 110° (Fig. S3, ESI†). 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 (Fig. S3, ESI†).
The mechanical properties of the spandex fiber such as tensile
stress had been well maintained after the oxygen plasma treat-
ment (Fig. S4, ESI†). 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 (Fig. 1d and e), 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 (Fig. 1f).
The strong connection among the soft PEA shells allowed the
microspheres to arrange effectively without obvious structure damage compared with the hard PS microspheres (Fig. S5, ESI†). It should be noted that hexagonally arranged microspheres could be obtained on a planar glass substrate (Fig. S6, ESI†), 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 structures 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 hydrophilicity 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 (Fig. S7a, ESI†), 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 (Fig. S7b, ESI†).

Thanks to the commercially available spandex fiber (Fig. 2a) and the efficient coating process, these MCFs could be continuously prepared. Fig. 2b and c 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 (Fig. 2d–f). The reflection peaks exhibited a linear relationship with the diameter of microspheres (Fig. S8, ESI†) in accordance with 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 (Fig. 2g and h), and these properties are 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 (Fig. 2g–i). Interestingly, although the fibers from the same core–shell microspheres showed a similar reflection peak position (Fig. S9, ESI†), 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 (Fig. S10, ESI†). In addition, this method is applicable to a variety of fiber shapes, and the circle, rectangle and triangle were studied as three demonstrations (Fig. 2j–l). Note that this preparation method could also be extended to the other shapes such as thin films (Fig. 2m) and textiles (Fig. 2n) besides fibers, and it was also found to be effective for various substrates such as glass (Fig. 2m).

Benefiting from the unique core–shell structure and elastic substrates, the MCFs exhibited reversible color changes under deformation. For instance, the MCFs switched colors from red to green and from green to blue under stretching (Fig. S11, ESI†). 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 (Fig. 3a), and the corresponding reflection peaks were gradually shifted from 554 to 495 nm (Fig. 3b and c). At the same time, the intensity decreased with increasing strains.

The main reflection position (λ) could be estimated by Bragg’s equation: \( \lambda = 2d(n_{\text{eff}}^2 - \sin^2 \theta)^{1/2} \), where \( \lambda \), \( d \), \( n_{\text{eff}} \) and \( \theta \) correspond...
to the reflection wavelength, the lattice spacing, the effective refractive index and the angle between the incident beam and the diffraction plane, respectively.\textsuperscript{35} For mechanochromic colloidal crystals based on an elastomer, the change of $d$ under strain is always accompanied by the change of $n_{\text{eff}}$. However, the change of $d$ causes a much more significant color shift than that of $n_{\text{eff}}$. Therefore, the effect of $n_{\text{eff}}$ is not emphasized when the structural colors are tuned by varying $d$.\textsuperscript{1,36} The structural change of the elastic colloidal crystals under deformation had been addressed in the previous work mainly based on the Poisson ratio and the rearrangement of microspheres.\textsuperscript{26,37,38}

To summarize, when the MCFs were axially elongated under stretching, the soft PEA shell deformed, and the thickness of the coated microsphere layer decreased in order to maintain the total volume constant, which caused the decrease in 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.\textsuperscript{29} As a result, the reflection peaks displayed a blue shift with decreased intensities under stretching.\textsuperscript{22,26,29,37}

Fig. 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.
Meanwhile, as the MCF elongated, the applied force also gradually increased during the blue shift of the reflection spectra (Fig. S12, ESI†). 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 changed, thus the reflection peak was invariable.29 After release, they could recover back to the original arrangement and show obvious optical response.

The chromatic transitions were also found to be reversible based on the reflection spectroscopy. The reflection peaks and intensities remained almost unchanged after stretching for over 2000 cycles (Fig. 3d and e). The high reversibility and repeatability were attributed to the unique structure of the MCFs with an elastic fiber in the core and a chromic layer in the sheath. For comparison, chromic fibers consisted of only core–shell microspheres were also prepared by using the melt extrusion process. The MCFs based on the dip-coating process required fewer microspheres but exhibited better mechanical properties than the melt-extruded fibers (Fig. S13, ESI†). For instance, after a drawing-and-releasing cycle with a strain of 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 100 cycles of deformation, while the extrusion-based fiber showed poor cyclic properties and broke off after tens of deformations. For practical application, the resistance to scrubbing was then tested via a standard laundry process in a washing machine. After washing, no significant structure damage was observed in the MCFs (Fig. S14, ESI†). Moreover, the structural color and the corresponding reflection spectra were also maintained before and after washing (Fig. S15, ESI†), 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 (Fig. 4a) and could be woven into a variety of textiles. For instance, they could be made into a hand chain (Fig. 4b) and a fabric (Fig. 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 (Fig. 4d). In addition, the mechanochromic behaviors of the building fibers allowed the resulting textiles to change their colors under deformation. For instance, the hand chain that was made from red fibers at middle and green fibers outside (Fig. 4e) switched the color of the middle fibers to green under stretching (Fig. 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 could be controlled by varying the diameters of the 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 could be 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 as a possible alternative to the traditional dyeing technique and has promising applications in the smart wearable textile industry.

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Fig. 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.

Notes and references