

# Fabrication of Structurally-Colored Fibers with Axial Core–Shell Structure via Electrophoretic Deposition and Their Optical Properties

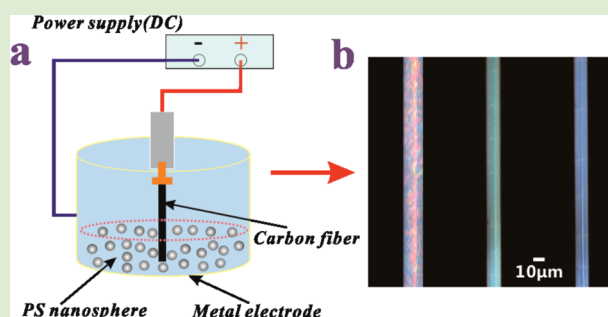
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## **S** Supporting Information

**ABSTRACT:** Structurally colored fibers were fabricated using different-sized polystyrene (PS) nanospheres via electrophoretic deposition on conductive carbon fiber surfaces. The reflective spectra corresponding to different colors were taken by microzone and angle-resolved spectrometers from a single colloidal fiber. As confirmed by structural analysis, the outer layer of the core–shell colloidal fibers consisted of face-centered cubic (f.c.c.) domains without long-range order. It is revealed that the absence of long-range order in the colloidal assembly caused isotropic reflection in radial and longitudinal directions on the colloidal fibers. Furthermore, due to the incorporation of random defects during growth process, the experimental spectra are blue-shifted and broad compared to reflective spectra calculations based on the curved f.c.c. structure. This technique is speculated to have potential application in structural coloration and radiation-proof fabrics.



Structural colors result from complex interactions between light and intricate nanospheres that are strongly reflected in the range of visible light spectra.<sup>1</sup> The nature of structural colors have evolved for over 515 million years,<sup>2</sup> with many wild flora and fauna displaying color due to periodic nanostructures. These nanostructures are configured as one-, two-, or three-dimensional photonic crystals on the skin or other parts of animals; they have been found in peacock feathers,<sup>3</sup> butterflies,<sup>4</sup> sea mice,<sup>5</sup> beetles,<sup>6</sup> birds,<sup>7</sup> and so on. The unique characteristics of this phenomenon, including high luminance, high saturation and resistance to fading, have recently caught the scientific community's attention. The remarkable, naturally occurring, structurally colored "clothes" will potentially revolutionize the textile industry by inspiring fabrication of colorful "clean textiles".

For the textile industry, dyeing is currently an essential process in the coloring of fabrics or fibers. However, dyeing causes severe water pollution due to contamination from residual colorants or pigments. These contaminants are difficult to degrade via chemical or biological methods.<sup>8–10</sup> Many new dyes and technologies<sup>11,12</sup> have been introduced in an attempt to reduce the pollution, but the sustainable development of modern textiles is impeded by pollution, high energy consumption, and low exploitation of fresh resources. To transcend this obstacle, a revolutionary method of coloring is required.

Structurally manufacturing textile coloration is a potential alternative to utilizing dyes. Using one of several techniques,

researchers have made great progress in artificially fabricating photonic structures similar to natural photonic crystals.<sup>13–16</sup> One of the most efficient processes is colloidal assembly,<sup>17</sup> which can be controlled by external fields.<sup>18,19</sup> In particular, physical confinement, gravitational sedimentation, and electrophoretic deposition (EPD) on colloidal crystal growth have been studied for several decades.<sup>20</sup> Due to its simplicity and effectiveness, the EPD method has been utilized most intensively to assemble colloidal particles on conductive substrates to form functional nanostructures.<sup>21–23</sup> However, cylindrical photonic structures in the fibrous shape are less researched despite potential application in the textile industry.

Recently, fiber-based devices based on the EPD technique, such as photovoltaic and electrically conductive fibers, have emerged as promising materials in energy conversion.<sup>24,25</sup> PS nanospheres with diameters of 460 and 660 nm were electrophoretically deposited on carbon fiber to form cylindrical colloidal crystals.<sup>26</sup> Subsequently, those cylindrical colloidal crystals were templates in the fabrication of inverse opals used in application to sensors and fuel battery electrodes.<sup>27,28</sup> Fibrous dye-sensitized solar cells were fabricated by coating TiO<sub>2</sub> nanoparticle thin films on stainless wire.<sup>29</sup> Tour et al.<sup>30</sup> succeeded in fabricating carbon nanotube and graphene nanoribbon-coated conductive kevlar fibers through layer-by-

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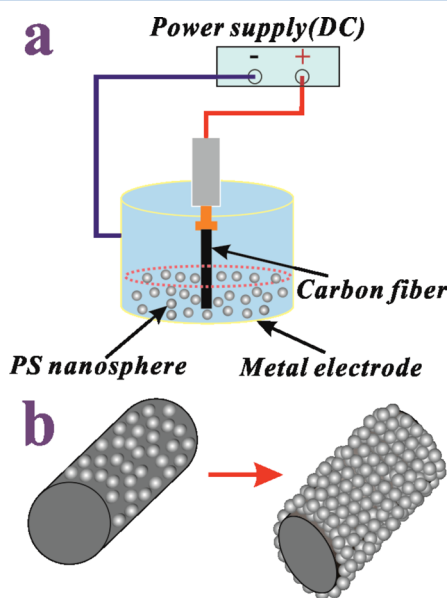
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layer spray coating. A fiber-based organic light-emitting device (OLED) capable of exhibiting an emission spectrum without the independence of the observing angle was constructed by Brendan et al.<sup>31</sup>

In this work, the EPD technique was adopted to fabricate core-shell colloidal fibers with structural colors. Colloidal spheres (100–300 nm in diameter) were selected as building blocks and electrophoretically assembled onto carbon fibers to obtain structural colors. The optical properties of the fibers were studied by microzone and angle-resolved spectrometers. The relation between the diameters of structurally colored fibers and imposed voltage was researched. Finally, two distinct numerical models were built to validate the experimental results and offer in-depth understanding on the optical properties of the colorful fibers.

Carbon fibers were fixed onto copper plates via conductive silver glue, as shown in Figure 1. Subsequently, voltages were



**Figure 1.** Fabrication of the structurally colored fibers. (a) Experimental set up of the EPD process. (b) Assembly of PS nanospheres on carbon fibers, controlled by electrophoresis.

imposed on the electrodes to drive the colloidal spheres to attach and assemble cylindrical colloidal structures on the surface of the carbon fibers. PS nanospheres with diameters of 185, 230, and 290 nm were selected to fabricate colorful core-shell fibers. According to the Bragg's Law, the photonic crystal assembled by the above PS spheres would present red, green, and blue colors with light normally incident on the (111) plane of the f.c.c. structure. Similar structural colors were expected to appear on the colloidal fibers. It was noted that the mechanical strength of the coated carbon fibers was unchanged, examined by the stress-strain curves (Figure S4, Supporting Information).

The optical dark-field images of colloidal fibers in red, green, and blue are shown in Figure 2a. The reflective spectra were measured by optical spectrometer as shown in Figure 2b. The peaks at 635, 525, and 435 nm corresponded to individual structural colors shown in Figure 2a. Surface and cross-sectional structures of colloidal fibers, consisting of PS nanospheres with diameters of 230 nm, are shown in Figure 2c,d. The arrangement of the colloidal nanospheres deviates from the

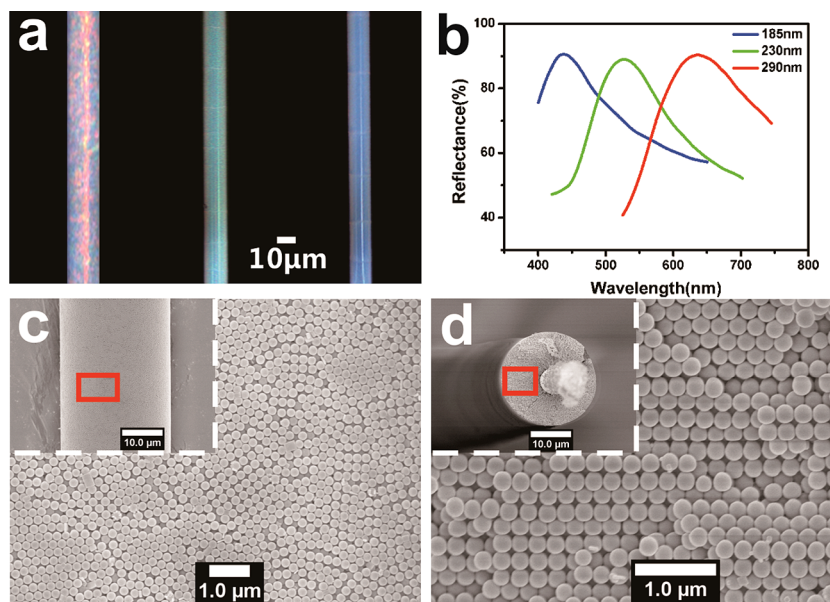
ideal f.c.c. structure. Ordered domains with sizes of 10–20  $\mu\text{m}^2$  are randomly oriented without the long-range order, as clearly observed from the enlarged surface and cross-sectional structures.

Figure 3 summarizes the growth dynamics of core-shell colloidal fibers as a function of applied voltage and deposition time during EPD. The diameters of the colloidal fibers increased with applied voltage in a fixed 80s duration, as shown in Figure 3a, clearly indicating that the growth rate of the colloidal fiber increases as a function of the applied voltage. Changes in the diameter of the colloidal fibers were monitored by varying the applied voltage and deposition time, as shown in Figure 3b. The diameter of the carbon fiber (7.0  $\mu\text{m}$ ) was constant within the duration of EPD until 120 s, when the applied voltage on the electrodes reached under 3.0 V. PS colloidal spheres were unable to be electrophoretically deposited on the carbon fibers if the imposed voltage was smaller than the threshold voltage (3.0 V). This is possibly due to the fact that the applied electric field is too weak to overcome the Brownian motion of the colloidal spheres, resulting in the spheres experiencing difficulty forming directional motion toward carbon fibers for deposition on the fiber surfaces. The diameters of the colloidal fibers increased when the deposition time under the larger voltage (>3.0 V) was incremented. However, the diameter of the colloidal fiber reached a plateau when the deposition time exceeded 80 s at 10 V. As the negatively charged colloidal particles were continuously deposited on the surface of the positive electrode (carbon fibers), the effective electric field at the vicinity of the fiber was screened until electrophoretic force exerted on the colloidal spheres balanced the Brownian motion, causing colloidal fibers to reach maximum diameter and stop growing. The above results are based on PS nanospheres with the diameter of 230 nm, with same results observed for diameters of 185 and 290 nm.

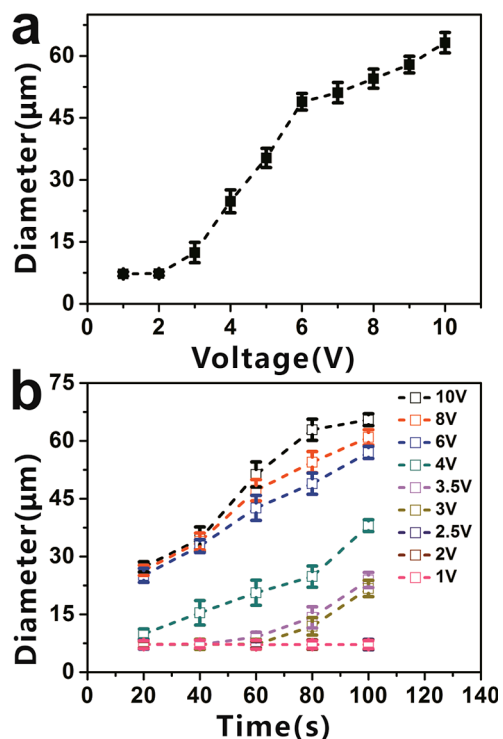
The obtained colloidal fibers consisted of core carbon fibers and outer layer of the colloidal assembly. To clearly describe the core-shell colloidal fibers, the value for fiber diameter is converted into number of colloidal layers. The empirical equation applied for the planar colloidal crystal is as follows:<sup>32</sup>

$$N = \frac{(T - r)}{r} \times \frac{3}{2\sqrt{6}} + 1 \quad (1)$$

where  $N$  is the number of layers,  $T$  is the thickness of the colloidal crystal, and  $r$  is the radius of PS nanospheres. Equation 1 is valid when  $r$  is approximated to be much smaller than the diameter of the core fiber, as the deposited layers are then approximately parallel to each other and the substrate surface (carbon fiber). Figure 4 illustrates the reflective spectra of core-shell fibers coated by varying thicknesses of colloidal layers, electrophoretically deposited by increasing the deposition time at a voltage of 10 V. According to eq 1, the numbers of colloidal layers correspond to 15, 17, 19, and 22, respectively. Interestingly, increasing the colloidal layers of the carbon fibers did not affect the reflective peaks of the different-sized fibers, indicating the number of colloidal layers minimally impact fiber coloration. Similar results have been demonstrated by Mohammad et al.<sup>33</sup> It is believed that light only interacts with a few of the outermost layers surrounding the carbon fibers, regardless the fineness of the fibers (Figure S5, Supporting Information).

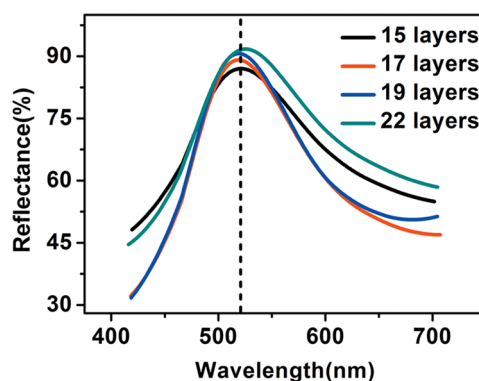


**Figure 2.** Optical property and structure of the structurally colored fibers. (a) Dark-field images of red, green and blue-colored fibers under the microscope. (b) Reflective spectra with corresponding peaks at 635, 525 and 435 nm corresponding to red, green and blue colors. (c) Surface and (d) cross-sectional SEM images of green fiber. Inset: images taken in the low magnification. The locations of the enlarged colloidal structures are marked in red.



**Figure 3.** Growth dynamics of colloidal fibers versus the imposed voltage. (a) Growth of the colorful fibers via voltage increase. (b) The diameters of fibers consisting of 230 nm diameter PS spheres changed with the deposition time under different voltages.

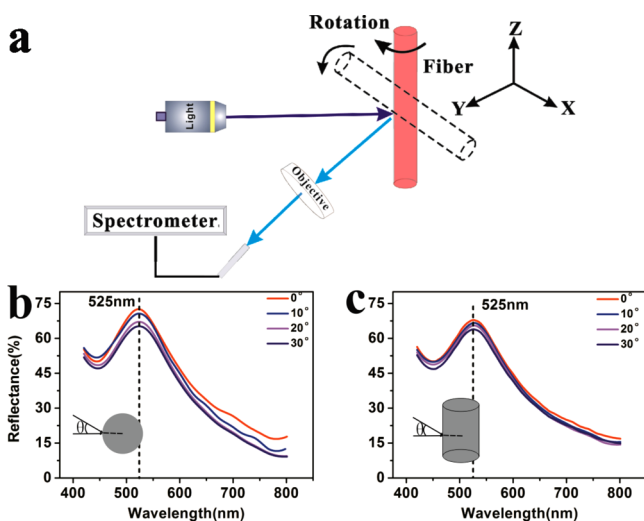
Subsequently, the optical properties of single fibers were studied by angle-resolved spectrometer (Figure S7, Supporting Information), as shown in Figure 5a. The reflections in the radial and longitudinal directions perpendicular to and along the fiber were measured by changing the incident angle of light. Figure 5b shows that the reflective spectra in the radial direction were independent of the incident angle of the light as



**Figure 4.** Spectra of structurally colored fibers with the different layers. The central peak position is 525 nm. The diameter of PS nanospheres is 230 nm.

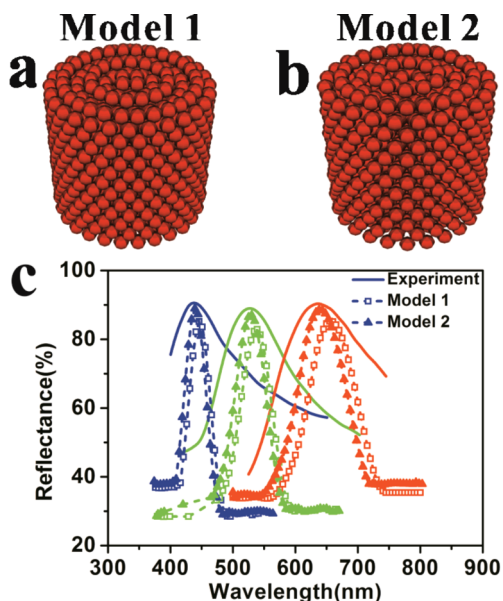
the incident angles changed from  $0^\circ$  to  $30^\circ$ . It was understood that the isotropic reflections were caused by cylindrical symmetry of the fibers, as shown in the inset figure of Figure 5b. Interestingly, the reflective spectra in the longitudinal direction are also independent to the angles of the incident light, as shown by the curves in Figure 5c. The SEM images in Figure 2c indicate that the assembly of the colloids consists of small crystalline domains with areas in the range of  $100\text{--}200\ \mu\text{m}^2$ . It is clear that the long-range order does not exist in the larger scale. This isotropic surface structure causes the omnidirectional reflection measured in the longitudinal direction. It is notable that this noniridescent effect, different from most natural and artificial structural colors, is significant to textile application due to the obtained color remaining constant at different viewing angles. Similar effects caused by long-range disorder photonic spongy structures have been found in parrot feathers.<sup>34</sup>

To validate the above results and offer an in-depth understanding of optical properties of dye-free colorful fibers, the reflective spectra of the colloidal fibers are calculated by the



**Figure 5.** The angle-resolved reflection of the colloidal fibers. (a) Schematic diagrams of the angle-resolved spectrometer for the measurements of reflective spectra. (b) Reflective spectra taken from direction perpendicular to the fibers. (c) Reflective spectra taken from longitudinal direction along the fibers. The fibers were deposited by the 230 nm colloidal spheres.

Rigorous Coupled Wave Analysis (RCWA) method.<sup>35</sup> The ideal structure of the computer-generated colloidal fiber is the curved f.c.c. structure shown in Figure 6a. The diameter of the



**Figure 6.** Comparison of the reflective spectra between the deposited fibers and ideal models. (a) The curved f.c.c. model, Model 1. (b) Modified model by increasing the lattice constant of the ideal structure, Model 2. (c) The reflective spectra of different models and deposited fibers.

modeling fibers is exactly 2  $\mu\text{m}$ . The periodic boundary condition along the longitudinal direction of the fibers was adopted in the calculation. The comparison between the experimental spectra and the calculation on Model 1 is made in Figure 6c. The experimental reflection peak is largely blue-shifted in terms of the ideal structure, particularly for the red color. Subsequently, the second model (Model 2) was constructed by increasing the lattice constant of Model 1.

The calculated spectra based on Model 2 were plotted as the curve with triangular points in Figure 6c. This plot has the same peak position as the experimental spectra. The lattice constant of Model 2 is 265 nm, which is 15% greater than that of Model 1 (230 nm). The represented blue-shifting is accomplished by increasing the lattice constant (more details in Figure S8, Supporting Information), as according to Bragg's Law. From above results, it can be concluded that the deposited fiber possesses incomplete crystalline structure deviating from f.c.c. structure. Compared to the ideal structure, the nonclose packing of the colloidal spheres on the surface of the fiber caused larger lattice constants and blue-shifting of the optical spectra. Moreover, peaks in the measured data were observed to be relatively broad compared to the calculated peaks. Many defects such as cracks and grain boundaries were found on the deposited fibers. Therefore, the broadening peaks could be attributed to light scattered by defects and imperfections in the colloidal fibers (Figure S6, Supporting Information).

In conclusion, the EPD technique was employed to fabricate structurally colored fibers with PS nanospheres. The reflective peaks corresponding to red, green, and blue colloidal fibers were assembled using colloidal spheres with diameters of 185, 230, and 290 nm, respectively, with measurements by optical spectrometer. The colors of the colloidal fibers were changed by simple variations in the sizes of the colloidal nanospheres. The growth dynamics of colloidal fibers through EPD were characterized as a function of imposed voltage and deposition time. Increasing the applied voltage or deposition time resulted in larger diameter (number of layers) of the colloidal fibers. It was determined that the reflective peaks (colors) are independent to the layers of the colloidal fibers since the visible light only interacts with the few outermost colloidal layers. The experimental spectra are blue-shifted and broader in comparison to the calculated reflective spectra based on the curved f.c.c. structure, due to incorporation of random defects during the EPD process. It is noteworthy that the isotropic reflections in the radial and longitudinal directions on the colloidal fibers are attributed to the lack of long-range order in their structures by using an angle-resolved spectrometer.

These findings are indicative of significant potential in the fabrication of dye-free colorful textiles. Additionally, this technique may be extended to applications in conductive mesh or fabrics. It is possible that conductive fabrics coated by colloidal photonic structures, in addition to displaying color under visible light, are opaque in infrared and ultraviolet wavelengths. This trait makes such textiles significant toward fabrication of radiation-proof fabrics, with applications toward shielding against exposure to electromagnetic radiation.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental materials, procedures and instrumentation, angle-resolved spectrometer, and details on numerical calculation. 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.

## ■ ACKNOWLEDGMENTS

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