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Facile fabrication of a magnetic induced structurally colored fiber and its strain-responsive properties

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An elastic structurally colored fiber with reversible structural color is described in this article. By using an external magnetic field, $Fe_3O_4@C$ superparamagnetic colloidal nanocrystal clusters (SCNCs) formed one dimensional chain-like photonic crystal structures and embedded in polyacrylamide matrix. When the fiber was stretched/squeezed in the horizontal direction, the size of fiber would be reduced/increased in the vertical direction. As a result, the distance between each sphere in chain-like structures can reversibly changed with the elastic deformation of the matrix, and the structurally colored fiber displays brilliant colors from red to green as the mechanical strain changes which can be read by the naked eye clearly. The peak of reflection can be tuned from 637nm to 515nm as a function of fiber extrusion or elongation. The novel structurally colored fiber is expected to have some important applications, such as the substitution of some fiber-based wearable electronic strain sensors because this fiber does not need any extra device to provide energy.

Introduction

Many creatures in nature, such as butterflies, sea mice, beetles, peacocks, display unique colors, which derives from periodic structures existed on their skin or other parts of their bodies.[1-4] It was called "structural colors". Structural colors have long been studied, owing to their unique characteristics and their applications as colorimetric chemical sensors, iridescent pigments, anticounterfeiting materials, and so on.[5-8] In order to acquire these structural colors artificially, various technological approaches have been developed, including colloidal particles self-assembly and interparticle repulsion-induced crystallization.[9-12] The fabrication of colloidal crystals through the method of colloidal particles self-assembly under the gravitational force[13], centrifugal force[14], electrophoretic deposition[15] and magnetic assembly[16-18] has been widely researched, especially the magnetic assembly technique to colloidal crystals. Compared to the other external force which are used as assemble the colloidal crystals, the magnetic induced colloidal particles assembly route has been believed one of the most fast and convenient method to fabricate the colloidal crystals.[19]

Structurally colored textiles, which imply those textiles with structural colors, have gained more and more interest because of their unique optical properties such as high luminance and resistance to fading.[20] Many researchers have done excellent works in this area. Diao et al. have demonstrated the fabrication of structurally colored textiles by embedding inverse opal structures in silk fabrics.[21] Zhou et al. reported the fabrication of structurally colored fibers by electrophoretic deposition on

conductive carbon fiber.[20] In our previous work, we also fabricated a structurally colored fiber based on photonic crystals in micro-space.[22] However, several problems still remain. Most structurally colored fibers are fabricated by assembling different layers of colloidal spheres onto the textiles or fibers, these structures are easy to be broken. Furthermore, once these structures are fabricated, it cannot be changed any more. These drawbacks severely limit the application of these fibers.

Recently, more and more researchers are focusing their attention on the area of wearable electronics, especially fiber-based wearable electronics.[23] One of the most important applications of these fiber-based wearable electronics is used for sensing, including humidity sensors,[24] chemical sensors[25-27] and gas sensors.[28] These fiber-based wearable electronics could also be used as strain or pressure sensors. However, there are some essential requirements for these flexible strain sensors, such as sensitive to strain; large strain measurement range; good repeatability in electromechanical response.[29] Therefore, the development of a practical method to prepare simple and energy-saving strain sensors still have an important demand.

Here, we propose a practical method for the creation of a novel structurally colored fiber by using a fast magnetically induced self-assembly technique. The superparamagnetic colloidal spheres are dispersed in polyacrylamide glycol gel matrix. Under the external magnetic field, one dimensional chain-like structure is embedded in the matrix. The distance between each sphere in chain-like structures can reversibly change with the elastic deformation of the matrix. The present structurally

colored fiber is expected to have some potential applications, such as the substitution of some fiber-based wearable electronic strain sensors because these fibers do not need any extra device to provide energy.

Experimental

Chemicals

Ferrocene ($\geq$98%), hydrogen peroxide ($\geq$30%), and acetone ($\geq$ 99%), acrylamide(AAm)($\geq$ 99%), N, N'-methylenebisacrylamid(MBAA)($\geq$ 99%), N, N, N',N-tetramethylethylenediamine(TEMED)($\geq$ 99%), ammonium persulfate (AP)($\geq$99%) and ethylene glycol(EG) ($\geq$99%) were purchased from Shanghai Chemical Factory, China. All chemicals were of analytical reagent grade and directly used without any further treatment.

Synthesis of Fe$_3$O$_4$@C superparamagnetic colloidal nanocrystal clusters(SCNCs)

In a typical experiment,[30] ferrocene(0.5g) was dissolved in acetone(60ml). After magnetic stirring for 15 min, hydrogen peroxide(2.0ml) was slowly added to the above solution. The mixture solution was vigorously stirred for 30 min. Then the obtained homogeneous solution was sealed in a Teflon-lined stainless autoclave (total volume 80ml) and heated at 180°Cfor 72h. After reaction, when the autoclave was cooled to room temperature, the products were isolated by a magnet and washed three times with acetone, and then dispersed in ethylene glycol with the concentration of 10mg/ml.

Synthesis of mechanical strain responsive structurally colored fibers

Inspired by Hu's work,[31] 1g acrylamide(AAm) was dissolved in 5ml ethylene glycol, then 0.01g ammonium persulfate and 0.02g N,N'-methylenebisacrylamid(MBAA) were added into the above solution to form a clear solution. After that, the mixture solution (1.5ml) was mixed with 0.5ml Fe$_3$O$_4$@C superparamagnetic colloidal nanocrystal clusters (SCNCs) which dispersed in ethylene glycol(EG) (10mg/ml). Then 10 μL N,N,N',N'-tetramethylethylenediamine(TEMED) was added into the above suspension. Finally, the final suspension was injected into a Teflon tube by using a syringe, under a permanent magnet with a magnetic field of 250mT, the structurally colored fiber was formed and was taken out of the Teflon tube.

Characterization

The particle size distribution was measured using a particle size and zeta potential analyzer (Malvern Nano85, England). Digital photos were taken by a digital camera (Nikon D7000, Japan). SEM images were recorded using a field emission scanning electron microscopy (FESEM) (Hitachi S-4800, Japan). TEM images were characterized using a transmission electron microscopy (JEOL-2100F, Japan). Reflection spectra of the structurally colored fiber were obtained using a fiber optic spectrometer (G2000-Pro-Ex, China). The incident light was aligned perpendicular to the fiber for all optical measurements.

Results and discussion

The superparamagnetic colloidal nanocrystal clusters (SCNCs) were produced by a hydrothermal reaction of ferrocene with acetone and hydrogen peroxide. After reaction, the uniform Fe$_3$O$_4$@C SCNCs were synthesized. Then the products were followed by washing several times with acetone and re-dispersed in ethylene glycol. The TEM images (Fig. S1) of the Fe$_3$O$_4$@C SCNCs revealed that the magnetic core was composed of dozens of primary iron oxide nanocrystals and an amorphous carbon shell was distributed on the surface of the magnetic core, the thickness of the carbon shell was about 25nm. The size distribution of Fe$_3$O$_4$@C SCNCs showed that the average particle size was about 290nm (Fig. S2). Fig. 1 (a) showed the digital photos of the Fe$_3$O$_4$@C SCNCs in ethylene glycol with concentration of 10 mg/ml, which displayed gray color when no external magnetic field was applied. When an external magnetic field was applied, the suspensions displayed
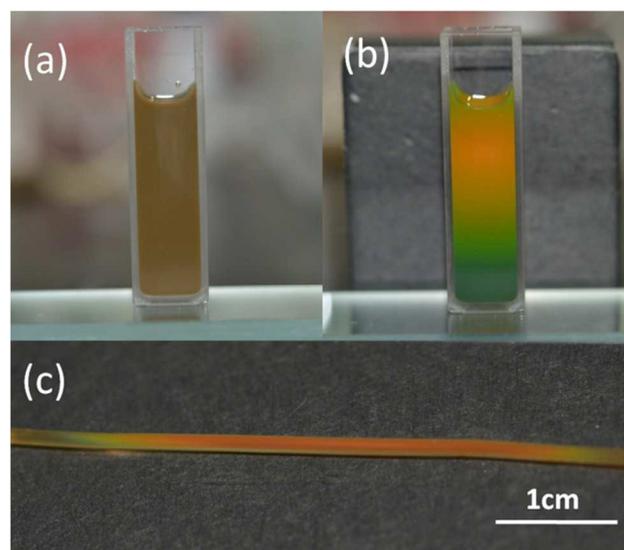

Fig.1 (a, b) Digital photos of the Fe$_3$O$_4$@C SCNCs in ethylene glycol. (a) No external magnetic field applied, (b) 250mT external magnetic field applied. (c) Digital photo of the structurally colored fiber fabricated in macro-space.

brilliant orange-red color at the top and green color at the bottom of the cuvette, this was mainly because the angle we observed was different (Fig. S3). According to previous studies, under the introduction of an external magnetic field, one dimensional chain-like photonic crystal structures based on these Fe$_3$O$_4$@C SCNCs were formed. Under the same external magnetic field, the center-center distance between each adjacent particle d was a constant, according to Bragg's law: $m\lambda=2nd\sin\theta$, m and 2n are also constant in the same system, the diffraction wavelength λ just depends on the angle (θ) we observed.[17, 32] Then 0.5mL solutions of Fe$_3$O$_4$@C SCNCs (10mg/mL) mixed with 1.5ml pre-gel solutions (1g AAm monomer powder, 20mg MBAA, 10mg AP were dissolved in

5mL EG) to form a new mixing solutions. After this, 10μL TEMED was added in the solutions, and then the solutions were injected into a Teflon tube using a syringe, at the same time, a magnet with a magnetic field of 250mT was placed at the bottom of the tube. A few seconds later, when the polymerization reaction was finished, the structurally colored fiber which consists of Fe_3O_4@C SCNCs forming the photonic structures was obtained. Fig. 1 (C) showed the digital photo of the structurally colored fiber which fabricated in macro-space. The structurally colored fiber displayed brilliant orange-red color under the background of black.

Fig. 2(a) and Fig. 2(b) demonstrated the SEM image of cross-section along the magnetic field of the structurally colored fiber. In parallel to the direction of the magnetic field, it can be clearly observed that the magnetic particles formed one dimensional chain-like structures inside the fiber. The reason that these particles formed one dimensional chain-like structures can be explained by the following equation:

$$F_2 = \nabla(\mathbf{m} \cdot \mathbf{H_1}) = 3(1-3\cos^2 \alpha)m^2/d^4 \cdot \mathbf{r}\ ^{33}$$

F_2 is the dipole force exerted on particle 2 induced by particle 1; $\mathbf{m}$ is a dipole moment along the direction of the external magnetic field, its induced magnetic field is $\mathbf{H_1}$; α is the angle between the external magnetic field and the line connecting the center of the two particles, its value ranging from 0° to 90°; d is the center-center distance from particle 1 to particle 2; $\mathbf{r}$ is the unit vector parallel to the line pointed from the center of particle 1 to that of particle 2. When the interaction between particle 1 and particle 2 approaches zero, we can calculate a critical angle of α is 54.09°. If $0° \leqslant \alpha < 54.09°$, the particle-particle interaction is attractive while repulsive if $54.09° < \alpha \leqslant 90°$. Under an external magnetic field, the dipole-dipole
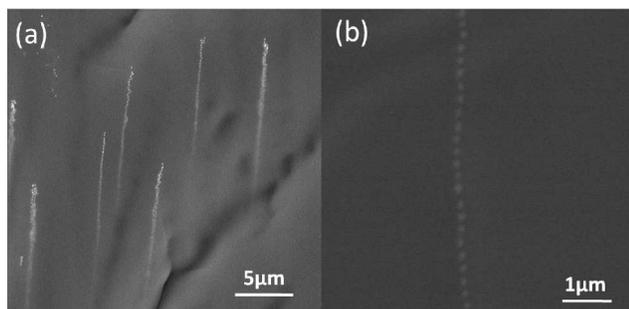

Fig. 2 (a, b) SEM images of a cross-section along the magnetic field of the structurally colored fiber, which show the magnetic particles forming chain-like structures inside the fiber.

interaction energy would be large enough to overcome thermal fluctuations, particles were driven to form one dimensional chain-like structure by the magnetic dipole-dipole force. When the magnetic field induced attraction was balanced by interparticle repulsions, a force equilibrium can be established, leading to a defined interparticle separation.[33]

It is known that the sensitivity was an important factor for evaluating the performance of strain sensors. Sensitivity can be characterized by the shift of the diffraction peak, the larger diffraction peak means a sharper color change. Fig. 3 showed the color changes of the structurally colored fiber by elongation or extrusion of the fiber due to mechanical strain.
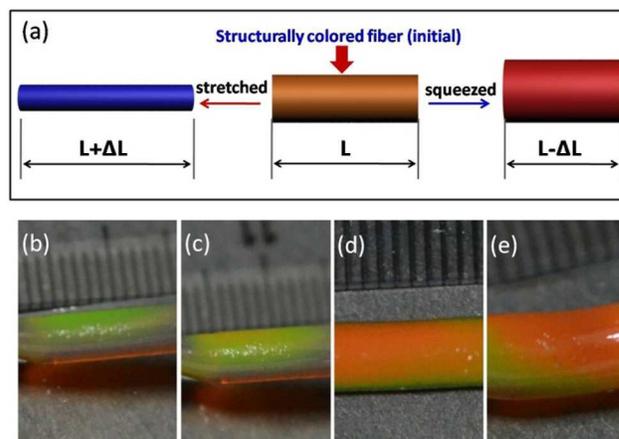

Fig. 3 Changes in the structural color of the structurally colored fiber by applying mechanical strain. (a) Elastic deformation when the structurally colored fiber is squeezed from L to L-△L and stretched from L to L+△L. (b, c) digital photos of the stretched structurally colored fiber (L+△L), (d) digital photo of the initial fiber (L), (e) digital photo of the squeezed fiber (L-△L).

Fig.3 (a) illustrated the different elastic deformations: the length of the structurally colored fiber from the initial value, L, to the stretched length, L+△L, or to the squeezed length, L-△L. Parts (b, c, d, e) of Fig. 3 were the digital photos of the stretched, initial and squeezed fiber, respectively. These digital photos show the structurally colored fiber displayed different colors when they were stretched or squeezed. On the initial fiber in Fig. 3 (d), the structural color was orange. When the fiber was stretched, as shown in Fig. 3 (b) and (c), the gradients in color were observed from orange to yellow-green to green. In contrast, when the fiber was squeezed, as shown in Fig. 3 (e), the color was observed from orange to red. After releasing the mechanical strain of the structurally colored fiber, the fiber can revert to its initial state. Furthermore, the whole process was reversible and repeatable by applying and releasing the mechanical strain.

The structural color of the fiber due to Bragg diffraction and its peak position corresponds to the elongation/extraction of the fiber. Fig. 4 (a) showed the changes of the reflectance spectrum of the fiber under different elongation or extrusion. The measurements were carried out in the circled process as shown in Fig. 3 (b, c, d, e). When the fiber was stretched, the peak position shifted from 607nm to 515nm, when the fiber was squeezed, the peak position shifted from 607nm to 637nm. Fig. 4 (b) shows the changes of the peak position at different ratio of △L/L. From the Fig. 4 (b), it can be concluded that the fiber has good flexibility and can be tuned from the ratio of -20% to 40%.
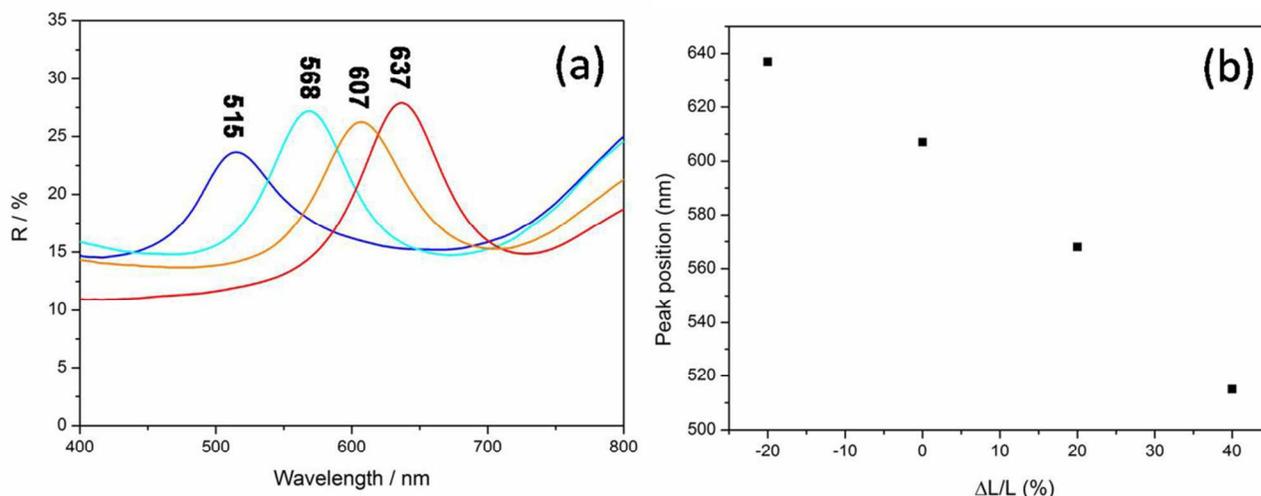
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Fig.4 Relationship between the peak positions and elongation or extrusion of the structurally colored fiber. (a) Reflectance of Bragg diffraction. (b) Peak position at different ratio of △L/L.

The reason that the structural colored fiber had such mechanical strain sensitivity can be explained by Fig. 5. The tuning color of the fiber depends on the lattice constant changing in the chain-like structures. As shown in Fig. 5, when the fiber was squeezed in the horizontal direction, the size of the fiber would increase in the vertical direction, leading to the increasing of the distance between each
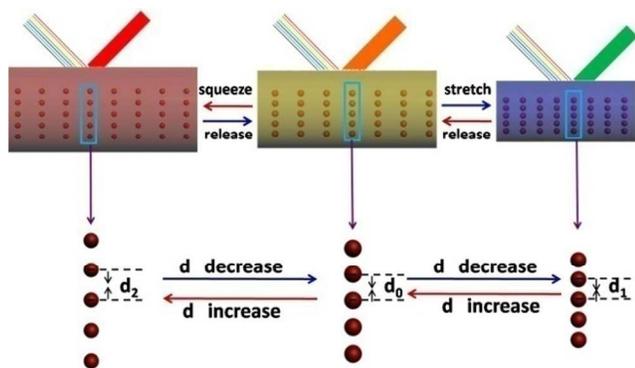

Fig. 5 A schematic illustration of the structurally colored fiber and the mechanism of the color change between different mechanical strain. d_0 is the interparticle spacing in chain-like structures of the initial fiber, d_1 is the interparticle spacing in chain-like structures when the fiber was strectched, and d_2 is the interparticle spacing in chain-like structures when the fiber was squeezed.

$Fe_3O_4@C$ SCNCs in chain-like structures. According to Bragg's law, $m\lambda=2nd\sin\theta$ (m is the diffraction order, λ is the wavelength of incident light, n is the effective refractive index,

d is the lattice spacing, and θ is the glancing angle between the incident light and diffraction crystal plane), [34] the increasing of the distance between each SCNCs bring d value increases from d_0 to d_2 and consequently red-shifts of the diffraction. By contrast, when the fiber was stretched in the horizontal direction, the size of fiber would decrease in the vertical direction, leading to the d value decreases from d_0 to d_1, brings the particles closer and blue-shifts of the diffraction. Therefore, the structurally colored fiber can achieve the colorimetric detection of mechanical strain based on displaying different colors by squeezing or stretching.

Conclusions

In summary, a structurally colored fiber that exhibits tunable and reversible structural color due to mechanical strain has been fabricated. This new magnetic-induced structurally colored fiber is expected to be useful for developing a new fiber-based mechanical strain sensor because of its self-display color tuning capability. Furthermore, this new structurally colored fiber holds great promise for the development of smart textiles device with novel external strain detections because it doesn't need any extra device to provide energy.

Acknowledgements

Notes and references

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