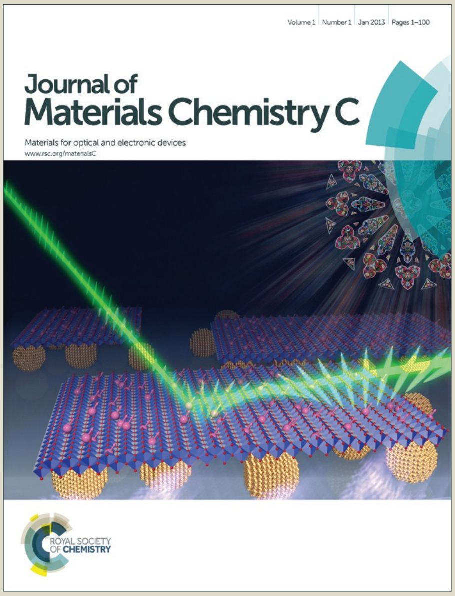
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Free-standing, flexible thermochromic films based on one-dimensional magnetic photonic crystals

Huiru Ma[a,b], Mingxing Zhu[b], Wei Luo[a], Wei Li[a], Kai Fang[a], Fangzhi Mou[a], Jianguo Guan[*a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We have in this paper developed a simple, one-stepwise strategy to fabricate free-standing, flexible thermochromic films in a centimeter scale by the instant free radical polymerization of steric-stabilized magnetically responsive photonic crystal (MRPC) nonaqueous suspension containing N-isopropyl acrylamide under an external magnetic field (*H*). In the as-prepared thermochromic films, the uniform superparamagnetic polyvinylpyrrolidone-coated Fe_3O_4 colloidal nanocrystalline cluster (Fe_3O_4@PVP CNC) particles exist as a form of one-dimensional (1D) nanochain-like photonic crystal structures parallel oriented along the direction of *H* in the poly(N-isopropyl acrylamide) (PNIPAM) gel matrix. Since the PNIPAM matrix has a much smaller refractive index than that of the Fe_3O_4@PVP CNC particles, and may remarkably change its volume and thus the lattice constants with temperature, the as-prepared thermochromic 1D PC films can display bright iridescent colors obviously sensitive to temperature with good reversibility and durability even when the volume fraction of the Fe_3O_4@PVP CNC particles is as low as 0.1 vol%. For example, the blue-shift range for the diffraction wavelength can reach up when temperature increases from 10 to 35 °C. Compared to the previously reported 3D photonic crystal films, they have also significant advantages of facile, instant one-stepwise preparation process and good mechanical properties. Furthermore, the lattice constants and optical properties can be conveniently tuned by altering *H* or cross linked level during the polymerization process. Therefore, the as-obtained self-standing thermochromic 1D PC films are believed to have a potential in the practical applications as a new generation of thermochromic polymer matrix composite materials.

Introduction

Photonic crystals (PCs) generally consist of at least two components of different refractive index in a periodic array, and include Bragg stack and colloidal crystalline arrays (CCA).[1-4] Among them, responsive PCs are able to change the periodical lattice spacing or the refractive index contrast, and thus modulate the color by various external stimuli, such as magnetic field,[5-7] electric field,[8, 9] ionic concentrations,[10, 11] temperature,[12-15] pH[16] and stress.[17-20] Therefore, they have important applications in different aspects of structural color printing and displays,[21-24] anti-counterfeiting devices,[25] optical devices,[28-30] outdoor signage, bioassays and sensors.[17, 19, 20, 31]

Thermochromic PCs formed by CCA are usually constructed by introducing temperature-responsive polymers such as poly(N-isopropyl acrylamide) (PNIPAM) into the periodic structures either as building blocks or as surrounding matrix. PNIPAM shows a lower critical solution temperature (LCST) or a volume phase temperature (VPT) at around 32 °C, and can make a reversible, rapid discontinuous change in volume between the swollen state and the collapsed state under external temperature stimuli,[32] resulting in the color tunability of its PCs. Similar to hard spheres, monodispersed PNIPAM-based microgel particles can self-assemble into CCA and exhibit a fast, reversible thermochromic property.[26-28] But these ordered CCA structures are generally disrupted at temperature near to or above the VPT, and do not display bright structural colors at temperature much lower than VPT because of the little refractive index contrast.[30] On the other hand, the hard CCA ordered structures immobilized in covalently cross-linked PNIPAM polymer networks may avoid the above mentioned shortcomings and exhibit structural colors changing with environmental temperatures.[29] Subsequently, to improve the color brightness and responsive rate of them, inverse opal PNIPAM hydrogels have also been developed by removing the regularly arranged colloidal polystyrene (PS) or silica (SiO_2) sphere templates.[33-36] However, it requires extreme technical acuity besides time-consuming and tedious process to fabricate these three dimensional (3D) opal or inverse opal thermochromic PCs, especially in a scale larger than centimeter size.[37] Moreover, as the continuous phase PNIPAM in the collapsed or swollen state has a refractive index different little from that of the colloidal crystals of PS, SiO_2 spheres or solutes, these 3D PCs only show strong diffraction peaks or bright iridescences at high colloidal particle concentrations. In this case, they still manifest an obviously diminishing diffraction intensity with temperature, and become very fragile, unsettled and hard to self-support once the substrates are removed due to the low filling fraction of PNIPAM.[38,39] This limits the practical applications of the thermochromic photonic crystals.

Different from 3D PCs, magnetically responsive photonic crystals (MRPCs) are composed of 1D chain-like parallel orientation structures with uniform space distances between neighboring monodispersed superparamagnetic particles adjustable by external magnetic field (*H*). They can display a variety of bright colors almost in the whole visible spectrum even if the superparamagnetic particles in the systems have a volume fraction as low as about 0.1 vol% due to its high refractive index.[7, 38-41] Thus, it offers a facile and plausible approach to develop a variety of sensors, display and anti-counterfeit technologies if the 1D photonic chains consisting of monodispersed superparamagnetic particles are fixed in a solidified polymer matrix.[22-25, 42- 45]

In this paper, taking account that the tunability in the structural color and particle distances by *H* is almost independent of the ionic strength or pH value for the steric-stabilized MRPCs,[7] we have demonstrated to fabricate a thermochromic 1D magnetic photonic crystal free-standing film by a facile free radical polymerization of steric-stabilized magnetically responsive photonic crystal (MRPC) nonaqueous suspensions containing NIPAM under a magnetic field. In the as-obtained free-standing films, superparamagnetic Fe_3O_4@PVP CNC particles are steadily fixed into parallel orientation chains by PNIPAM polymer networks with a uniform distance between neighboring particles, which determines the initiative iridescence. Owing to the great refractive index contrast to the PNIPAM matrix and low volume fraction of the superparamagnetic Fe_3O_4@PVP CNC particles, the as-obtained films not only exhibit reversible and bright structural colors sensitive to temperature ranging from 10 to 35 ^{o}C, but also are flexible and do not need any substrates to support. This is significantly advantageous over the previously reported 3D opal and inverse opal thermochromic hydrogels. Furthermore, changing the magnetic field strength and crosslinking agent content used in the polymerization can conveniently tune the premier lattice constant and the color tunable range. Compared to the self-standing flexible polymer 1D PC films based on nanoparticle multilayers,[46, 47] the as-obtained thermochromic photonic cystal self-standing films have supplementary advantages of the one-stepwise rapid preparation process and the convenient tunability of optical properties. Therefore, they are expected to hold a promise for the practical applications as a new generation of thermochromic polymer-based materials due to the long cycle lifetime and excellent mechanical properties.

Experimental section

Chemicals

N-isopropylacrylamide (NIPAM, ≥ 98%), N, N'-methylene-bis-acrylamide (MBAAM, ≥ 99%), ammonium persulfate (APS, ≥ 99%), tetramethylethylenediamine (TEMED, ≥ 99%), ethylene glycol (EG, ≥ 99%) and absolute ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd., China and used as received. Uniform superparamagnetic polyvinyl pyrrolidone-coated Fe_3O_4 colloidal nanocrystalline cluster (Fe_3O_4@PVP CNC) particles with a diameter (*D*) of about 150 nm were synthesized by a one-pot solvothermal polyol process according to our previous report,[7] and characterized by SEM and TEM in Fig. S1.

Fabrication of free-standing thermochromic 1D photonic crystal films

The free-standing thermochromic 1D photonic crystal films were fabricated by an instant radical polymerization process under an external magnetic field. In a typical process, we added 2.5 mg monodispersed superparamagnetic Fe_3O_4@PVP CNC particles, 0.18 g NIPAM, 7.4 mg MBAAM（3 mol% of NIPAM） and 14.4 mg APS into 0.3g of ethanol and EG (1:1) solution and ultrasonically dissolved them until a brown homogeneous solution was formed. Then into the solution, 15 µL TEMED catalyst was added and rapidly stirred for 10 s at room temperature. Afterward, the mixed solution was quickly sandwiched between two quartz plates to modulate the shape and size of the resultant film (25 mm × 25 mm × 0.5 mm), under which a round NdFeB permanent magnet (D10 × 1 cm) was placed to afford an external magnetic field (*H*) of about 90 Gauss upon the solution. In such a way, the superparamagnetic Fe_3O_4@PVP CNC particles in the solution were self-assembled into 1D photonic crystal chains, resulting in a bright iridescence before the polymerization. About 3~5 min late, the solution was solidified. The thermochromic 1D photonic crystal free-standing film was obtained by simply peeling the solidified sample from the quartz substrate, then washing it using deionized water for 3 times to remove the water-soluble substances including ethanol and EG and finally immersing it into water.

To obtain the thermochromic 1D photonic crystal free-standing films with different initiative colors, one could repeat the above experiments but the content of the crosslinking agent MBAAM or the intensity of *H* upon the NIPAM solution prior to gelation were altered. All of the resultant film samples were preserved in water at room temperature before use.

Sample characterization

The digital photos of the thermochromic free-standing film were obtained using a Nikon D7000 digital camera. A Hitachi S4800 scanning electron microscope (SEM) was used to investigate the distribution morphologies of the superparamagnetic Fe_3O_4@PVP CNC particles in the photonic crystal free-standing films. The compositions of the films were studied by Fourier-transformed infrared (FTIR) spectrometer and the thermal analyzer. The FTIR spectrum were obtained using a 60-SXB FTIR spectrometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Thermal analysis was conducted on a NETZSCH-STA449C/G under air at a heating rate of 10 ^{o}C·min^{-1}. In order to measure the content of absorbed water (C_{H_2O}) of PNIPAM gel, the film was immersed in deionized water overnight at a given temperature. After taken away from water and wiped off excess water on its surface, the film was weighted and recorded as W_1. Then it was weighted again and recorded as W_2 after dried in a vacuum oven at 100 ^{o}C for 1 hour. The content of absorbed water was calculated according to the formula:

$$C_{H_2O} = \frac{W_1 - W_2}{W_2}$$

Measurement and numerical simulation of optical properties

The diffraction spectra were all measured by Ocean Optics USB-2000 UV-vis spectrometer coupled to a six-around-one reflection probe. All reflections were measured with normal incidence and reflection and temperature was controlled through a circulated water bath control system. The distance between the samples and light probe is set to be 1 cm.

The simulated optical properties are calculated using a Finite Element Method (FEM) based commercial package Comsol Multiphysics in a wavelength range from 400 to 800 nm. In a typical model, a certain amount of spherical particles with a diameter (2*a*) of 150 nm are embeded in a dielectric matrix with a cross section area of 400 × 400 nm and arranged in a straight chain with a uniform space distance between the neighboring particles. They form a tetragonal column structure containing a particle chain. A plane wave is excited from one end of the column and propagate along the chain. Absorbing boundary conditions are used for all sides. The electric fields at the wave exciting end are recorded and are used to calculate the reflection.

Results and discussion

The free-standing thermochromic 1D photonic crystal films can be simply prepared by a one-step instant radical polymerization of monomer solutions containing NIPAM and monodispersed superparamagnetic Fe_3O_4@PVP CNC particles under an external magnetic field. Figs. 1a and b are the digital photos of the representative thermochromic photonic crystal free-standing film in the forms of plane and bend. Evidently, the film displays a homogeneous bright red color, which is changeable depending on bending degrees or incident angles. This suggests that its colors have the iridescent nature and are resulted from the strong diffractions of visible light by the regular periodic structures of photonic crystals in the PNIPAM film. The as-obtained free-standing film has a good mechanical property and can be bended at will, suggesting that it is more flexible than the conventional thermochromic PC films based on polystyrene (PS) or SiO_2 CCA templates.

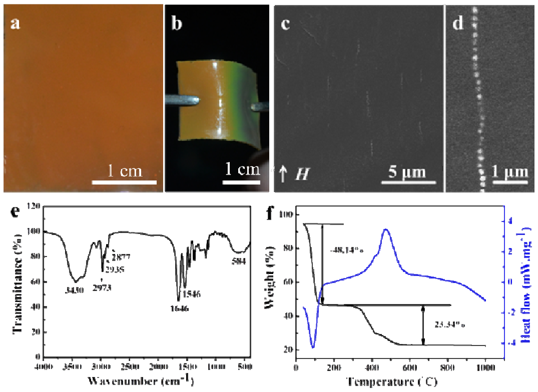


Fig. 1 Characterization of the typical free-standing thermochromic 1D PC film: digital photos of the (a) plane and (b) bending film; (c, d) SEM images of a cross-section along the direction of the external magnetic field applied before the polymerization; (e) FT-IR spectra and (f) TG-DSC curves in air

As present in Fig. 1c, there appear a small number of isolated 1D chain-like structures in the completely dried film. They have a length of several micrometers and are arranged in parallel along the external magnetic field. Fig. 1d clearly reveals that the 1D chain-like structure consists of about 150-nm-sized particles with an almost uniform space distance between the neighboring particles, confirming that the superparamagnetic Fe_3O_4@PVP CNC particles are assembled into chain-like PC structures under *H*, and fixed by the PNIPAM polymer networks. This is because the Fe_3O_4@PVP CNC particles have a PVP shell and can be stabilized in solution by the steric hindrance effect, which is insensitive to the ionic strength in solutions.[7] Thus the chain-like structures formed by the self-assembly of the Fe_3O_4@PVP CNC particles under *H* are not destroyed in the free radical polymerization. More importantly, they can steadily remain in the solidified polymer films when the PNIPAM films are in the swollen state or near at the VPT. The few number of the isolated 1D chain-like structures in the dried film is consistent with the fact that the charged ratio of the Fe_3O_4@PVP CNC particles into the polymerizable monomer is less than 0.1 wt%. However, the as-obtained 1D PC film can still manifest bright structural colors besides the excellent mechanical properties including bending performance when it is properly crosslinked. This is quite different from the previously 3D opal and inverse opal PC hydrogels, which have strong diffraction peaks or bright iridescences only at high colloidal particle concentrations. Such excellent optical and mechanical properties of the as-obtained magnetic PC free-standing films can be ascribed to the assumption that in the well order 1D chain-like photonic crystal structures the refractive index contrast between the Fe_3O_4@PVP CNC particles and the surrounding PNIPAN matrix is large enough to diffract visible light effectively.

Fig. 1e gives the FTIR spectrum of the film. It shows the characteristic peaks of PNIPAM at 1664 cm^{-1} (–C=O stretching), at 1546 cm^{-1} (-N-H stretching) and the characteristic peak of Fe_3O_4@PVP CNC particles at 580 cm^{-1} (Fe-O vibration) respectively. In addition, the broad band at 3430 cm^{-1} is attributed to the bending vibration of N-H in PNIPAM. This is in accordance with the film composition including PNIPAM and Fe_3O_4@PVP CNC particles. Fig. 1f displays the TG-DSC curves of the film in air. The TG curve indicates that the as-obtained 1D PC film has two differentiated steps of weight loss in the temperature range of 40-1000 ^{o}C. Accompanied with an endothermic peak at 100 ^{o}C in DSC curve, the first steep weight loss occurred at 40-105 ^{o}C is followed with a smooth platform at 105-300 ^{o}C. This is due to the evaporation of the water adsorbed inside the PNIPAM hydrogel network. The weight loss in this stage reaches 48.14%. The second weight loss of 23.34% begins at about 300 ^{o}C, and ended at around 600 ^{o}C. It corresponds to an exothermic wavelength at 500 ^{o}C. This is ascribed to the partial oxidation or insufficient combustion of the PNIPAM gel polymer. From the DSC-TGA curves, it is clear that the as-obtained 1D PC gel film shows a strong water absorption capability, illustrating a robust expansion and shrinkage performance, which benefits the wide tunability in the lattice parameter.

Reflection spectra at different temperatures were measured to evaluate the thermochromic property of the as-obtained 1D PC free-standing film. Fig. 2a reveals that the as-obtained 1D PC free-standing film displays a variety of remarkable diffraction peaks and bright iridescent colors at different temperatures (*T*), implying that changing *T* does not damage the ordered structure of the 1D PC chains in this temperature range. With T decreasing from 35 to 10 °C, the Bragg wavelength (λ_{max}), which corresponds to the diffraction peak, red-shifts from 660 nm to 520 nm. The digital photos of the 1D PC film at several temperatures were also taken, as represented in Fig. 2b, which shows that both its structural colors and volume are remarkably dependent on T. With T decreasing from 35 °C to 10 °C, the film volume expands gradually and the color changes from green at 35 °C, via yellow at 28 °C, orange red at 23 °C and then to red color at 10 °C. This is imaginable since decreasing T will make the PNIPAM matrix transform from the hydrophobicity into the hydrophilicity, and significantly improve the water absorption capability. Fig. 3 indicates that when the PC film immersed in water was heated from 10 °C into 50 °C, the content of absorbed water (C_{H2O}) first decreased gradually, then sharply at 30-40 °C. Above 40 °C, it again decreased slowly. This suggests that the VPT of the free-standing film occurs at 30-40 °C. The free-standing film has C_{H2O} up to 3.50 g/g at 10 °C, more than twice of that at 40 °C (1.41 g/g), illustrating the obvious increment of the PNIPAM hydrogel volume with decreasing T, which is regarded to be responsible for the increase of the space distance between the neighboring magnetic particles (T_s) or lattice constant ($d = 2a + T_s$, $2a$ is the diameter of Fe_3O_4@PVP CNC particle) in the chain-like structures. According to Bragg diffraction law, for the normal incidence the Bragg wavelength $\lambda = 2nd$. Here n is the refractive index of the 1D PC films based on the PNIPAM hydrogels, and can be approximated as $n = n_{PNIPAM} m_{PNIPAM} + n_{water} m_{water}$ as the content of the Fe_3O_4@PVP CNC particles is very low and the density of PNIPAM polymer is almost equal to that of water. n_{PNIPAM} and n_{water} are the refractive indices of PNIPAM (1.50) and water (1.33), respectively. m_{PNIPAM} and m_{water} are the mass fraction of PNIPAM and water, and can be calculated by $m_{PNIPAM} = 1/\left(C_{H_2O}+1\right)$ and $m_{water} = C_{H_2O}/\left(C_{H_2O}+1\right)$. Therefore, decreasing T leads to the red-shift of the diffraction wavelength.

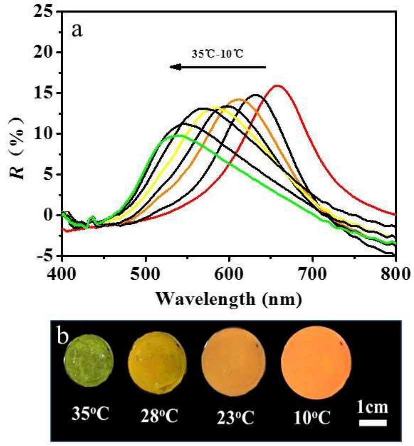


Fig. 2 Reflection spectra (a) and digital photographs (b) of the as-obtained free-standing thermochromic 1D PC film at different temperatures.

Using the measured diffraction wavelength and Bragg diffraction law, we can obtain d and T_s of the as-obtained 1D PC film at different T. The blue line in Fig. 3 correlates the relationship between T_s and C_{H2O}. It seems that near or below VPT of the as-obtained 1D PC film (for example, in the case of T from 10 to 35 °C), the d and T_s increases linearly rather than in a cubic root fashion with increasing C_{H2O}, as indicated by the blue dash line in Fig. 3. The linear correlation coefficient between T_s and C_{H2O} reaches up to 0.9986. This suggests that the PNIPAM polymer hydrogels confined between magnetic particles mainly swell in one direction parallel to the axial direction of the 1D particle chain-like structures. It is understandable if one considers that the magnetic particles, which occupy most of the volume of the 1D particle chain-like structures, do not response to temperature changes. Thus, the PNIPAM polymer hydrogels confined between magnetic particles have to contract/swell in one direction in order to match with the volume changes of the surrounding responsive PNIPAM polymer hydrogels.

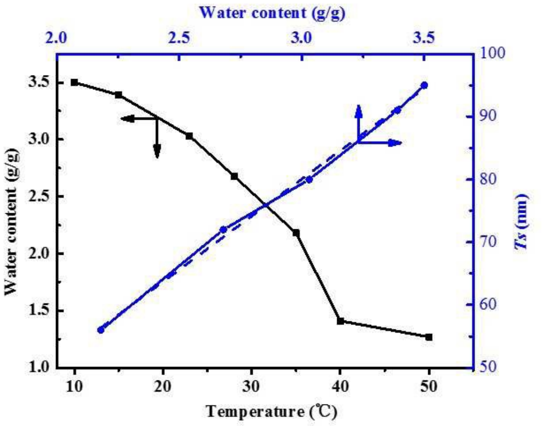


Fig. 3 Temperature dependence of the absorbed water content (black line) and the influence of the absorbed water content on T_s (blue line) for the as-obtained free-standing thermochromic 1D PC film.

It is worth noting that for the as-obtained 1D PC film, all the diffraction intensities does not weaken distinctly and the structural colors keep bright almost in the whole investigated temperature range. This is because the Fe_3O_4@PVP CNC particles in the 1D PC chains have a large refractive index (2.42), much higher than those of the PNIPAM matrix in both the swollen and collapsed states (1.33 ~ 1.50). As a result, a remarkable Bragg diffraction certainly occurs either in the swollen or the collapsed state of the PNIPAM hydrogels. In contrast, the previously reported thermochromic 3D opal PC hydrogels based on PS or SiO_2 spheres in the PNIPAM matrix usually show weak diffraction peaks at the collapsed state, while those of the monodispersed PNIPAM-based microgel particles or the inverse opal thermochromic PCs generally display illegible iridescences at the fully swollen state due to the low refractive index contrast between the periodical building blocks and surroundings.

It is also noted from Fig. 2a that the as-obtained 1D PC film at different temperatures shows the reflection spectra with a large full width at half maximum (FWHM) and limited reflection intensity at λ_{max}, even though it contains numerous particle chains in the thickness direction, and the particle chain length in it reaches about 5 μm or above, as indicated by Fig. 1c and d. In contrast, ideal photonic crystals could have perfect square like spactra. This deviation may come from several factors, such as the size distribution of the particles, perturbation in the particle spacing, the chain curvation, as well as the insufficient layers or chain length (L). In order to confirm this, we have made some numerical simulations using FEM based commercial package Comsol Multiphysics. Fig. S1 represents the simulated reflection spectra of a PNIPAM tetragonal column hydrogel containing a single photonic crystal chain with various neighboring interparticle distances. It reveals that λ_{max} monotonously increases and a maximum value in the peak intensity occurs with increasing d. This is in line with the experimental results indicated in Fig. 2a. Furthermore, as expected, the reflection peaks become sharp and the FWHM distinctively narrows. However, the peak intensity is still very limited in this case. To furthermore verify that the low peak intensity is closely associated with L, Fig. S2 shows the reflection spectra of a single photonic crystal chain with different L. It can be seen that lengthening L remarkably enhances the peak intensity. At L of 15 μm, the reflectance reaches 30% at λ_{max}. All these simulated results clearly illustrate that improving the monodispersity of the particle size and d, as well as lengthening L or increasing the layer number of particle chains are all beneficial for the achievement of perfect reflectance.

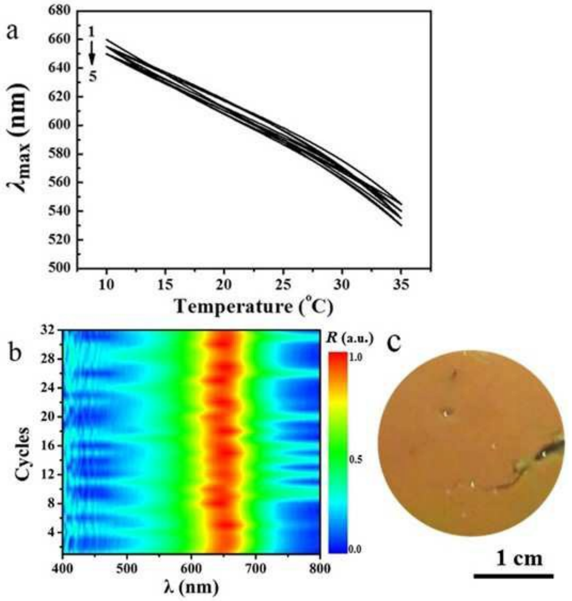


Fig. 4 The cyclic curves of the diffraction wavelength *versus* temperature (a), reflection spectra at 10 °C *versus* cycle times (b) and the digital photo after 32 cycle times (c) for the as-obtained free-standing thermochromic 1D PC film. A cycle refers to firstly raising temperature from 10 to 35 °C and then falling temperature to 10 °C. During each cycle, the sample is at least kept at 10 and 35 °C for more than 30 min to get stable reflection spectra after the thermal equilibrium.

The reversibility and stability is another aspect of the thermosensitivity for the as-obtained thermochromic 1D PC free-standing film. Accordingly, 5 successive experiments of λ *versus* T have been carried out using the as-obtained thermochromic 1D PC free-standing film. The procedure of namely firstly raising temperature from 10 °C to 23 °C, 28 °C, 35 °C and then falling temperature to 28 °C, 23 °C and ending at 10 °C is adopted as one cycling. The results are recorded in Fig. 4a, which indicates that to a certain extent, the diffraction wavelengths are closed to each other. In all 5 cycling experiments, the response time during the heating process is shorter than that during the cooling process. With increasing the amount of cycles, the full width at half maximum of the diffraction peak almost fluctuates within a range of no more than 10 nm, suggesting a negligible relaxation behavior of the PNIPAM-based 1D PC film. The swelling and shrinkage of the PNIPAM matrix can keep up well with the temperature variation during the operational cyclic process. The good sensitivity and stability of the as-obtained thermochromic film may be attributed to the proper crosslinking degree of the PNIPAM matrix, the 1D chain-like PC structures and the free-standing ability. It is known that a polymer chain may easily stretch or shrink at a low crosslinking degree due to its low cohesion. The as-obtained 1D PC free-standing film has adequate free spaces for the PNIPAM matrix to adjust the conformation by swelling or shrinking due to the low content of building blocks besides the elimination of substrates. Consequently, it shows a quick and stable response to temperature stimulus. It should be noted that only when the as-obtained thermochromic film adsorbs adequate water can it respond to temperature. If the as-obtained film with a size of 25 × 25 × 0.5 mm is left in air at 15 °C and 42 % humidity, it will completely lose the structural color after 8 h, but will gradually display the original structural color if putting back into the original water surroundings again.

To estimate the service lifetime of the as-obtained 1D thermochromic film, we have measured the reflection spectra versus cycle times of the typical sample in water by alternatively tuning temperature between 10 and 35 °C. Fig. 4b demonstrates that both the diffraction intensity and the Bragg wavelength of the film at 10 °C hardly change with cycle times in our experiment range of 32 cycles. However, as imaged in Fig. 4c, the thermochromic film appears to crack at this time because of the repeated, abrupt and alternative expansion and contraction. These results manifest that the optical properties and 1D photonic crystal structures keep well in the final film. The key to prolong the service lifetime of the thermochromic film is to further improve its fatigue properties, which may be realized by adjusting the molecular structures including crosslinking level of the PNIPAM matrix.

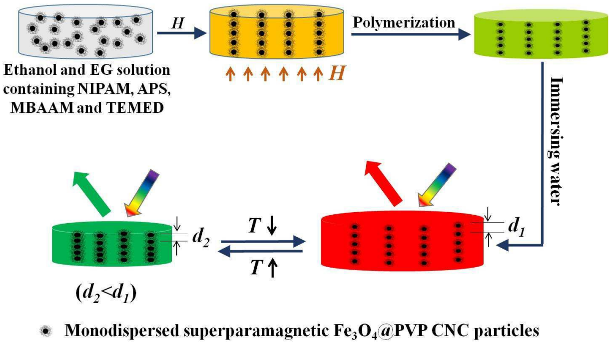


Fig. 5 The schematic illustration of the preparation route of the free-standing thermochromic 1D phonic crystal film as well as the mechanism of the color changing with temperature.

On the basis of the above discussion, we have proposed a schematic illustration of the preparation route and thermochromic mechanism for the free-standing 1D photonic crystal film as shown in Fig. 5. In our protocol, superparamagnetic Fe_3O_4@PVP CNC particles are dispersed uniformly in an ethanol and EG (1:1) solution containing NIPAM, APS, MBAAM and TEMED. Upon the application of external magnetic field (H), the superparamagnetic particles are aligned along the H direction into 1D chain-like photonic crystal structures, which can be conveniently and quickly fixed in a PNIPAM polymer hydrogel matrix via an instant free radical polymerization of NIPAM monomers as the steric repulsion between the superparamagnetic Fe_3O_4@PVP CNC particles is insensitive to ionic strength. In this way, flexible and free-standing 1D photonic crystal films are prepared. The structural color is somewhat different before and after the polymerization reaction of NIPAM. This possibly results from the volume shrinkage caused by the solidification of NIPAM monomers. The as-obtained 1D PC free-standing film has an obvious transition between hydrophilicity and hydrophobicity when temperature changes between 10 ^oC and 35 ^oC, leading to the tunability in volume as well as lattice constant (d). As a result, the diffraction wavelengths or iridescent colors change with varying T, following Bragg diffraction law. For example, the color of the as-obtained 1D PC film can continuously turn from red to green when T gradually increases from 10 ^oC to 35 ^oC, and turn back to red again when T changes from 35 ^oC to 10 ^oC.

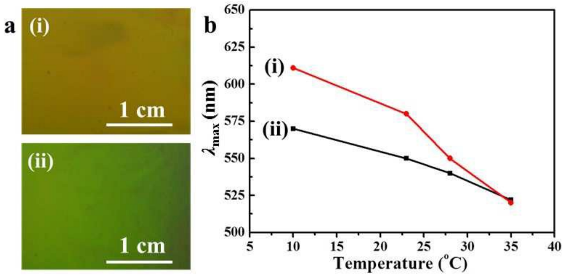


Fig. 6 The digital photos (a) and thermochromic curves (b) of the PNIPAM-based 1D photonic crystal films prepared at 3 mol% crosslinking agent and different H of 161 Gs (i) and 427 Gs (ii), respectively.

For the as-prepared free-standing 1D PC thermochromic films by one-step process, the interparticle distance in the 1D chain-like structures or lattice constant d can be conveniently modulated by the magnitude of H and judged by the structural color via naked eyes. Before the polymerization of the solutions containing monomer NIPAM, the superparamagnetic Fe_3O_4@PVP CNC particles can be assembled into magnetically responsive photonic crystals (MRPCs) upon the application of H due to the balance between the magnetic attraction and the steric repulsion. In this case, H dominates the lattice constant of MRPCs, and thus has a strong influence on d or the initiative structural colors of the resultant 1D PC free-standing films. Compared to Fig. 2b, Fig. 6 shows that the resultant 1D PC free-standing films with different initiative colors of orange red and green at 10 ^oC were fabricated in a centimeter scale when H was changed from 90 Gs to 161 and 427 Gs, respectively. This suggests the initiative lattice constants of the 1D PC films are modulated to be smaller. It is reasonable that under a relatively weak H, the Fe_3O_4@PVP CNC particles are assembled at a relatively large interparticle distance since the weak magnetic attraction between particles only need a weak steric repulsion to counter balance. In this condition, the polymer PVP shells of the superparamagnetic Fe_3O_4@PVP CNC particles are only slightly compressed. Thus, the 1D chain-like PC structures with a large d are fixed in the film, resulting in a red color. Increasing H strengthens the magnetic attraction exerted on the magnetic particles, which requires a strong steric repulsive force induced by the compression of flexible PVP macromolecular chains to match. As a result, the 1D chain-like PC structures with a small d are fixed in the film to diffract green light. Comparison of Fig. 2 and 6b reveals that similar to the 1D PC free-standing film prepared under H = 90 Gs, the diffraction wavelengths for those prepared under H = 161 and 427 Gs both make obvious blue-shifts when T is increased from 10 ^oC to 35 ^oC. All the 3 films almost have the same diffraction wavelength at 35 ^oC, but have quite different one at 10 ^oC. The color tunable ranges of them become narrow with augmenting H. For the green film obtained under 427 Gs, the diffraction wavelength can only change within a range between 570 nm and 523 nm. This is because once the superparamagnetic Fe_3O_4@PVP CNC particles are immobilized by the solidified PNIPAM polymers, the distances between the neighboring particles or the lattice constants of the 1D PC structures are hardly influenced by magnetic attraction, but determined by the volume of the PNIPAM hydrogels inserted between the magnetic particles. With increasing T, the PNIPAM hydrogel matrix shrinks due to the occurrence of the hydrophilic-hydrophobic transition, resulting in the lessening of the interparticle distance (d) and the blue-shift of the λ_{max}. As the film obtained under a weak H has a larger volume of the PNIPAM hydrogels inserted between the magnetic particles than that under strong H, the absolute value of the d tunability with T becomes more obvious, leading to a broad color tunable range. For the 3 kinds of the films, the PNIPAM hydrogels, which are all obtained at the same condition and cured with 3 mol% crosslinking agent, possess a C_{H2O} of bigger than 300% at 10 ^oC as shown in Fig. 3. Thus the spaces between the neighboring magnetic particles seem the same when the PNIPAM hydrogels are in the collapsed state, producing a similar diffraction wavelength at 35 ^oC.

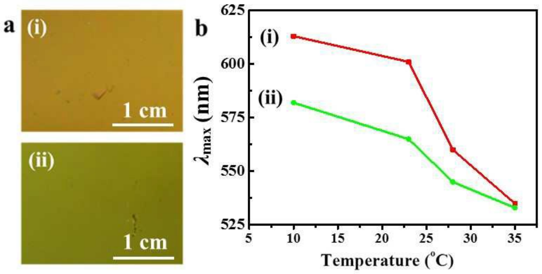


Fig. 7 The digital photos (a) and thermochromic properties (b) of the 1D PC free-standing films obtained at 90 Gs and different MBAAM contents of 4 mol% (i) and 5 mol% (ii).

The crosslinking of polymers makes a pronounced shrinkage and has a strong influence on the conformational changes, and thus plays a key role in the tunability of the hydrogel volume as well as the thermochromic properties of their-based PC films. Fig. 7 shows the digital photos and thermochromic properties of the 1D PC films cured by 4 mol% or 5 mol% MBAAM. In comparison of Fig. 2, it can be seen that with increasing the MBAAM content used in the polymerization, the initiative d at 10 ^oC decreases to some extents, as indicated by the blue-shift of the iridescence from red to orange red and yellow green color.

This can be reasonably explained by the assumption that with increasing the cross-link level of the polymer gels, a greater contraction will produce in the PNIPAM matrix, which reduces the interparticle distance. In addition, the color tunable range with T also becomes narrow when the MBAAM content used in the polymerization increases. Polymers with a proper cross-link level are usually elastomeric and there is enough free space in polymer networks for the polymer chains to expand or contract by absorbing or expelling water. This makes its-based PC film show iridescences in a broad visible spectrum. Increasing the cross-link level will depress the free space of the polymer chain, and limit the expansion by absorbing water at 10 ^{o}C, leading to both the changes of d and the shift of diffraction color and $\lambda_{\max}$, in a small range.

Conclusions

In summary, the free-standing, flexible thermochromic films based on 1D magnetic photonic crystals have been fabricated in a large scale by the instant radical polymerization of a steric-stabilized MRPC suspension containing NIPAM under an external magnetic field. In the as-prepared PNIPAM films, the superparamagnetic Fe_3O_4@PVP CNC particles are steadily fixed by the thermosensitive PNIPAM hydrogels in a form of parallel oriented 1D chain-like structures with an almost equal space distance between the neighboring particles. They can display bright iridescent colors sensitive to temperature ranging from 10 ^{o}C to 35 ^{o}C with good reversibility and durability due to the large refractive index contrast between the PNIPAM matrix and the Fe_3O_4@PVP CNC particles. Besides the facile, instant one-stepwise preparation process and the good mechanical properties, the as-obtained 1D PC thermochromic films have also remarkable advantages in the tunability of lattice constants and optical properties by conveniently changing the external magnetic field strength or the cross linked level of PNIPAM, producing different initiative colors and thermochromic ranges. Therefore, we believe that the results reported here pave a way for the practical applications of the thermochromic photonic crystal materials.

Acknowledgments

We acknowledge the financial support from the National Natural Science Foundation of China (51303143 and 21474078), the top talents lead cultivation project of Hubei Province, the Yellow Crane talent plan of Wuhan municipal government, the open funds of state key laboratory of advanced technology for materials synthesis and processing, Wuhan University of Technology (2014-KF-13), and the Fundamental Research Funds for the Central Universities (WUT: 2014-Ia-10).

Notes and references

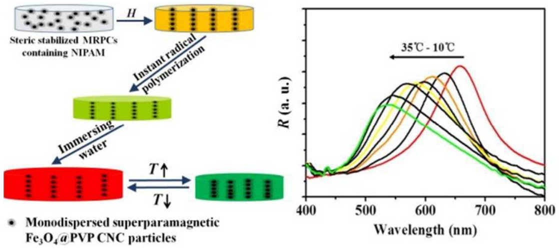
[a] *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China. Tel: +86-27-87218832; Fax: +86-27-87879468. E-mail address: guanjg@whut.edu.cn*

[b] *Department of Chemistry, School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan 430070, China*

1. A. Chiappini, A. Chiasera, S. Berneschi, C. Armellini, A. Carpentiero, M. Mazzola, E. Moser, S. Varas, G. C. Righini, M. Ferrari, *J. Sol-gel Sci. Technol.*, 2011, **60**, 408-425;
2. J. F. Galisteo-Lopez, M. Ibisate, R. Sapienza, L. S. Froufe-Perez, A. Blanco, C. Lopez, *Adv. Mater.*, 2011, **23**, 30-69;
3. Y. Takeoka, *J. Mater. Chem. C*, 2013, **1**, 6059-6074;
4. S. Zhao, D. Xu, H. Ma, Z. Sun, J. Guan, *J. Colloid Interf. Sci.*, 2012, **388**: 40–46;
5. J. Ge, Y. Yin, *Adv. Mater.*, 2008, **20**, 3485-3491;
6. X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, S. A. Asher, *Adv. Mater.*, 2001, **13**, 1681-1684;
7. W. Luo, H. Ma, F. Mou, M. Zhu, J. Yan, J. Guan, *Adv. Mater.*, 2014, **26**, 1058-1064;
8. A. C. Arsenault, D. P. Puzzo, I. Manners, G. A. Ozin, *Nat. Photonics*, 2007, **1**, 468-472;
9. J. Liu, Y. Mao, J. Ge, *J. Mater. Chem.C*, 2013, **1**, 6129-6135;
10. C. E. Reese, S. A. Asher, *Anal. Chem.*, 2003, **75**, 3915-3918;
11. H. Saito, Y. Takeoka, M. Watanabe, *Chem. Commun.*, 2003, 2126-2127;
12. J. D. Debord, S. Eustis, S. Byul Debord, M. T. Lofye, L. A. Lyon, *Adv. Mater.*, 2002, **14**, 658-662;
13. G. Huang, Z. Hu, *Macromolecules*, 2007, **40**, 3749-3756;
14. J. Zhou, G. Wang, M. Marquez, Z. Hu, *Soft Matter*, 2009, **5**, 820-826;
15. A. Seeboth, D. Lötzsch, R. Ruhmann, O. Muehling, *Chem. Rev.* 2014, **114**, 3037-3068;
16. Y. J. Lee, P. V. Braun, *Adv. Mater.*, 2003, **15**, 563-566;
17. C. I. Aguirre, E. Reguera, A. Stein, *Adv. Funct. Mater.*, 2010, **20**, 2565-2578;
18. H. Fudouzi, T. Sawada, *Langmuir*, 2006, **22**, 1365-1368;
19. J. H. Holtz, S. A. Asher, *Nature*, 1997, **389**, 829-832;
20. Y. Zhao, X. Zhao, J. Hu, J. Li, W. Xu, Z. Gu, *Angew. Chem. Int. Ed.*, 2009, **48**, 7350-7352;
21. H. Fudouzi, Y. Xia, *Langmuir*, 2003, **19**, 9653-9660;
22. J. Ge, J. Goebl, L. He, Z. Lu, Y. Yin, *Adv. Mater.*, 2009, **21**, 4259-4264;
23. H. Hu, Q. Chen, H. Wang, R. Li, W. Zhong, *J. Mater. Chem.*, 2011, **21**, 13062-13067;
24. R. Xuan, J. Ge, *J. Mater. Chem.*, 2012, **22**, 367-372;
25. H. Hu, Q. Chen, J. Tang, X. Hu, X. Zhou, *J. Mater. Chem.*, 2012, **22**, 11048-11053;
26. J. Gao, Z. Hu, *Langmuir*, 2002, **18**, 1360-1367;
27. Z. Hu, G. Huang, *Angew. Chem. Int. Ed.*, 2003, **42**, 4799-4802;
28. L. A. Lyon, J. D. Debord, S. B. Debord, C. D. Jones, J. G. McGrath, M. J. Serpe, *J. Phys. Chem. B*, 2004, **108**, 19099-19108;
29. J. M. Weissman, H. B. Sunkara, S. T. Albert, S. A. Asher, *Science*, 1996, **274**, 959-963;
30. E. Reese, A.V. Mikhonin, M. Kamenjicki, A. Tikhonov, A. Asher. *J. Am. Chem. Soc*., 2004, **126**, 1493-1496;
31. C. Fenzl, T. Hirsch, O. S. Wolfbeis. *Angew. Chem. Int. Ed.* 2014, 53, 3318 – 3335;
32. R. Pelton, *Adv. Colloid Interf. Sci.*, 2000, **85,** 1-33;
33. Z. Hu, X. Lu, J. Gao, *Adv. Mater.*, 2001, **13**, 1708-1712;
34. K. Matsubara, M. Watanabe, Y. Takeoka, *Angew. Chem. Int. Ed.*, 2007, **46**, 1688-1692;
35. Y. Takeoka, M. Watanabe, *Langmuir*, 2003, **19**, 9104-9106;
36. K. Ueno, K. Matsubara, M. Watanabe, Y. Takeoka, *Adv. Mater.*, 2007, **19**, 2807-2812;
37. C. E. Reese, C. D. Guerrero, J. M. Weissman, K. Lee, S. A. Asher, *J. Colloid Interf. Sci*, 2000, **232**, 76-80;
38. J. H. Holtz, J. S. W. Holtz, C. H. Munro, S. A. Asher, *Anal. Chem.*, 1998, **70**, 780-791;
39. J. Wang, Y. Cao, Y. Feng, F. Yin, J. Gao, *Adv. Mater.*, 2007, **19**, 3865-3871;
40. L. He, M. Wang, J. Ge, Y. Yin, *Accounts. Chem. Res.*, 2012, **45**, 1431-1440;
41. H. Kim, J. Ge, J. Kim, S.-e. Choi, H. Lee, H. Lee, W. Park, Y. Yin, S. Kwon, *Nat. Photonics*, 2009, **3**, 534-540;
42. H. Hu, H. Zhong, C. Chen, Q. Chen, *J. Mater. Chem. C*, 2014, **2**, 3695-3702;
43. R. Xuan, Q. Wu, Y. Yin, J. Ge, *J. Mater. Chem.*, 2011, **21**, 3672-3676;
44. J. Ge, Y. Yin, *Angew. Chem. Int. Ed.*, 2011, **50**, 1492-522.

45. X. Wang, C. Wang, Z. Zhou, S. Chen, *Adv. Optical Mater.* 2014, **2**, 652–662
46. M. E. Calvo, O. S. Sobrado, G. Lozano, H. Míguez, *J. Mater. Chem.*, 2009, **19**, 3144–3148
47. J. R. C. Smirnov , M. E. Calvo , and H Míguez, *Adv. Funct. Mater.* 2013, **23**, 2805–2811

TOC



An instant radical polymerization of steric-stabilized magnetically responsive photonic crystal nonaqueous suspension under an external magnetic field has been developed to fabricate flexible thermochromic free-standing films, where a low volume fraction of parallell oriented one-dimensional nanochain-like photonic crystal structures are steadily fixed in the poly(N-isopropyl acrylamide) gel matrix, displaying bright iridescent colors strongly sensitive to temperature with good reversibility and durability.