

Magneto-chromatic Microspheres: Rotating Photonic Crystals

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Abstract: Magneto-chromatic microspheres have been fabricated through instant assembly of superparamagnetic (SPM) colloidal particles inside emulsion droplets of UV curable resin followed by an immediate UV curing process to polymerize the droplets and fix the ordered structures. When dispersed in the liquid droplets, superparamagnetic Fe₃O₄@SiO₂ core/shell particles self-organize under the balanced interaction of repulsive and attractive forces to form one-dimensional chains, each of which contains periodically arranged particles diffracting visible light and displaying field-tunable colors. UV initiated polymerization of the oligomers of the resin fixes the periodic structures inside the droplet microspheres and retains the diffraction property. Because the superparamagnetic chains tend to align themselves along the field direction, it is very convenient to control the orientation of such photonic microspheres and, accordingly, their diffractive colors, by changing the orientation of the crystal lattice relative to the incident light using magnetic fields. The excellent stability together with the capability of fast on/off switching of the diffraction by magnetic fields makes the system suitable for applications such as color display, rewritable signage, and sensors. As a simple demonstration, we have fabricated a display unit that has on/off bistable states by embedding the magneto-chromatic microspheres in a matrix that can thermally switch between solid and liquid phases.

Introduction

Photonic crystal materials with a band gap property responsive to external stimuli have important applications in bio- and chemical sensors, color paints and inks, reflective display units, optical filters and switches, and many other active optical components.^{1–9} Colloidal crystals, which can be produced conveniently by self-assembling uniform colloidal particles, have been particularly useful for making responsive photonic materials because active components can be incorporated into the crystalline lattice during or after the assembly process. The majority of research in the field therefore has been focused on tuning the photonic properties of colloidal systems through changes in the refractive indices, lattice constants, or spatial symmetry of the colloidal arrays upon the application of external stimuli such as chemical change, temperature variation, mechanical forces, electrical or magnetic fields, or light.^{6–26} However, wide use of these systems in practical applications is usually hampered by slow and complicated fabrication pro-

cesses, limited tunability, slow response to the external stimuli, and difficulty of device integration.

Because the photonic band gap is highly dependent on the angle between the incident light and lattice planes, an alternative route to tunable photonic materials is to use external stimuli to change the orientation of a photonic crystal. For easy fabrication, actuation, and broader applications, it is highly desirable that the photonic crystals can be divided into many smaller parts whose orientation can be controlled individually or collectively as needed by using external stimuli. Photonic crystal microspheres, or “opal balls”, have been previously demonstrated by Velev et al. in a number of pioneering works by using monodisperse silica or polystyrene beads as the building

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blocks.^{27,28} The brilliant colors associated with these three-dimensional periodic structures, however, cannot be tuned due to lack of control over the orientation of the microspheres. Xia et al. have introduced magnetic components into a photonic microcrystal so that its diffraction can be changed by rotating the sample using external magnetic fields.²⁹ However, it has not been demonstrated that one can synthesize multiple copies of such photonic crystals, align them synchronically, and collectively output uniform color signals.

Among all potential external stimuli, a magnetic field has the benefits of contactless control, instant action, and easy integration into electronic devices, though it has only been used limitedly in assembling and tuning colloidal crystals due to the complication of the forces that are involved.^{30–32} Recently, we have developed a series of magnetically tunable photonic crystal systems through the assembly of uniform superparamagnetic (SPM) colloidal particles in liquid media with various polarities.^{33–37} The key to the successful assembly of such photonic crystals is the establishment of balance between the magnetically induced dipolar attraction and the repulsions resulted from surface charge or other structural factors such as the overlap of solvation layers. This finely tuned dynamic equilibrium leads to the self-assembly of the magnetic colloids in the form of chain structures with defined internal periodicity along the direction of external field and also renders the system a fast, fully reversible optical response across the visible–near-infrared range when the external magnetic field is manipulated.

In this paper, we report a new type of magnetically responsive photonic system—photonic crystal microspheres whose orientation and consequently photonic property can be easily controlled by using external magnetic fields. Specifically, the fabrication of microspheres involves instant assembly of SPM colloidal particles inside emulsion droplets of UV curable resin and then an immediate UV curing process to polymerize the droplets and fix the ordered structures. Unlike the previously reported “opal balls” whose orientation cannot be controlled, fixing of SPM chains makes microspheres magnetically “polarized” so that their

orientation becomes fully tunable as the SPM chains always tend to align along the external field direction. Many copies of photonic crystal microspheres can be fabricated in a single process, and their orientation can be synchronically tuned to collectively display a uniform color. Compared to the magnetically tunable photonic crystals that we reported previously, the photonic microsphere system does not involve the nanoparticle assembly step and, therefore, has several advantages including long-term stability of optical response, improved tolerance to environmental variances such as ionic strength and solvent hydrophobicity, and greater convenience for incorporation into many liquid or solid matrices without the need of complicated surface modification. For example, as will be demonstrated later in this paper, the magnetochromatic microspheres can be simply incorporated into a matrix, which can thermally change between liquid and solid phases, to produce a switchable color display system whose color information can be switched “on” and “off” multiple times by means of an applied magnetic field.

Experimental Section

Chemicals. Iron(III) chloride anhydrous (FeCl_3 , 98%) was purchased from Riedel-de Haën, German. Diethylene glycol (DEG, reagent grade), ethyl alcohol (denatured), hexane (99.9%), and sodium hydroxide (NaOH, 98.8%) were purchased from Fisher Scientific. Ammonium hydroxide solution (28%) was obtained from Fluka. Poly(acrylic acid) (PAA, $M_w = 1800$), tetraethylorthosilicate (TEOS, 98%), poly(ethylene glycol) diacrylate (PEGDA, $M_n = 700$), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), mineral oil (heavy), and silicone oil (Dow Corning Corporation 200fluid, viscosity 1000 cSt) were purchased from Sigma-Aldrich. Poly(ethylene glycol) ($M_w = 1500$) was obtained from Acros Organics.

Synthesis of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ Microspheres. Fe_3O_4 superparamagnetic colloidal nanocrystal clusters were synthesized by using a high-temperature hydrolysis reaction.^{36–38} $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ core/shell colloids were then prepared through a modified Stöber process. The magnetic colloids and photoinitiator DMPA (5 wt %) were dispersed in PEGDA-700 to form a brown homogeneous solution with a Fe_3O_4 concentration of 8 mg/mL. In a typical process, 1.5 mL of PEGDA precursor solution were mixed with 21 mL of mineral oil by vortex. The mixture was immediately transferred to a Petri dish on a 2" × 2" × 0.5" rectangular magnet and exposed to a UV lamp (Spectroline SB-100P, 365 nm) for 2 min at a distance of 2 cm from the bulb. After curing, the microspheres were washed with hexane and ethanol in sequence. The very few aggregations produced in the synthesis and microspheres larger than 200 μm were removed through gravity sedimentation in a mixture solution of DEG and Glycerol (20%). Finally, the microspheres were dispersed in 2 mL of DEG.

Characterization. A Tecnai T12 transmission electron microscope (TEM) was used to characterize the morphology of the core/shell colloids. A Philips FEI XL30 scanning electron microscope (SEM) was used to investigate the surface morphology of the microspheres. A Zeiss AXIO Imager optical microscope was used to observe the “on”/“off” state of diffraction from $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ microspheres when the magnetic field is rotated. The diffraction spectra in Figure 10 were measured by an Ocean Optics HR2000CG-UV-NIR spectrometer coupled to a six-around-one reflection/backscattering probe. The probe was perpendicular to the glass cell.

Measurement of Diffraction at Different Tilting Angles. As shown in Figure S1, a 100 W halogen light source with a collimation part at the end, a strip magnet with tunable angle, and an optical microscope connected with a spectrometer were set up to investigate the influence of tilting angle (θ) on diffraction peak wavelength

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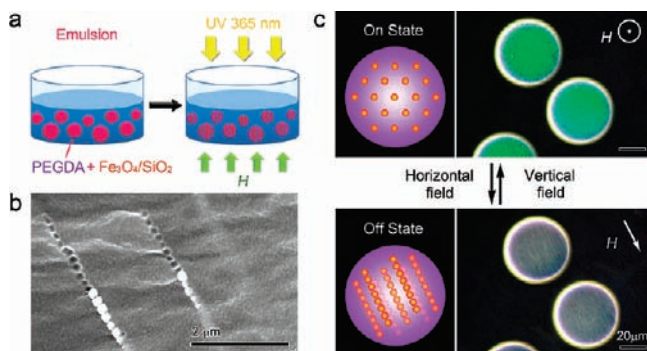


Figure 1. (a) Synthetic procedures for the magnetochromatic microspheres. When dispersed as emulsion droplets, superparamagnetic Fe₃O₄@SiO₂ core/shell particles self-organize under the balanced interaction of repulsive and attractive forces to form one-dimensional chains, each of which contains periodically arranged particles diffracting visible light and displaying field-tunable colors. UV initiated polymerization of the oligomers in emulsion droplets fixes the periodic structures inside the microspheres and retains the diffraction property. (b) SEM images of Fe₃O₄@SiO₂ particle chains embedded in a PEGDA matrix. (c) Schematic illustrations and optical microscopy images for the magnetochromatic effect caused by rotating the chain-like photonic structures in magnetic fields.

and intensity. The research object is a single Fe₃O₄@SiO₂/PEGDA microsphere trapped inside a PEGDA microcage in a PDMS microfluidic channel (Figure S2). The angle of the magnetic field was tuned within the plane constructed by the incident light and viewing direction, when the spectrometer and digital camera equipped on the microscope recorded the diffraction corresponding to every tilting angle (θ). The diffraction intensity (R) is defined as the ratio of reflection signal with microsphere to that without microsphere.

Measurement of Turning Threshold. Fe₃O₄@SiO₂/PEGDA microspheres were dispersed in a density matched solvent—PEGDA liquid with a low concentration. The dispersion was sandwiched between two hydrophobic cover glasses to avoid adhesion to the glass substrate and placed on the platform of a microscope. A 0.5" × 0.5" × 0.1" rectangular magnet was fixed right beneath the sample, and the magnetic field was tuned from 20 to 500 G with a step of 40 G by gently raising the magnet approaching the sample. The microspheres gradually turn on as the magnetic field increases, and the digital camera took photos (Figure 7) every step after the microspheres reached equilibrium in 5 s. The turning of viewable area was counted to plot the dependence of turning percentage on the field strength.

Measurement of Turning Frequency. Turning frequency of the microspheres was measured by a test platform built with a 100 W halogen white light source, a spectrometer, and a rotating magnet unit with a geared DC motor as shown in Figure S6. The microspheres were dispersed in PEGDA liquid and loaded onto a 5 mm × 5 mm wide and 1 mm deep glass cell, placed directly on top of the magnet. The rotating plate with NS and SN magnets standing alternately will produce a periodical vertical (1100–1200 G) and horizontal magnetic field (300–400 G), whose frequency is simply controlled by the rotational speed of the plate. By changing the frequency of the alternating magnetic field, the turning frequency changes accordingly, and the dependence of diffraction on time was mapped by the spectrometer.

Results and Discussion

The synthetic procedure of magnetochromatic microspheres is illustrated in Figure 1a. The Fe₃O₄ SPM particles are first coated with a thin layer of silica so that they can be well-dispersed in a liquid UV curable resin containing mainly poly(ethylene glycol) diacrylate (PEGDA) oligomers and a trace amount of photoinitiator 2,2-dimethoxy-2-phenylacetophenone

(DMPA). Dispersion of the Fe₃O₄/PEGDA mixture in a viscous nonpolar solvent such as silicone oil or mineral oil under mechanical stirring leads to the formation of an emulsion. Upon the application of an external magnetic field, the SPM particles self-assemble into ordered structures inside the emulsion droplets when the magnetically induced attraction reaches a balance with repulsive interactions including electrostatic and solvation forces.³⁶ An immediate 365-nm UV illumination quickly polymerizes the PEGDA oligomers to transform the emulsion droplets into solid polymer microspheres and, at the same time, permanently fixes the periodic SPM structures.³⁸ Consistent with the magnetically tunable photonic crystal systems that we reported previously,³⁶ microspheres with different colors can be obtained by controlling the periodicity of the SPM assembly through the variation of the external magnetic field during the UV curing process. Due to the short-range nature of the solvation force, the range of color that can be produced from a single Fe₃O₄/PEGDA mixture is limited.³⁶ A more practical method to produce microspheres with largely different colors such as red and blue is to use Fe₃O₄ particles with different initial sizes or with SiO₂ coatings of different thicknesses. The diameter of the microspheres typically ranges from 10 to 100 μm, depending on the type of oil and the speed of mechanical stirring. The fixation of the periodic SPM particles in the cured polymer matrix has been verified by inspecting a section that is cut from a sample along the chain direction. As shown in the scanning electron microscopy (SEM) image in Figure 1b, parallel particle chains with regular interparticle spacing can be easily observed, providing direct support of the one-dimensional ordering of the SPM particles proposed in previous studies.^{32,35,37} Since the cutting is not strictly along the chain direction, usually part of the chain is embedded inside the polymer and part of it has been peeled off, leaving behind regular cavities. Consistent with our prior observation, the separation between neighboring chains is typically on the order of a few micrometers due to the strong interchain repulsion induced by the external field.³⁵

The diffraction of the microspheres dispersed in a liquid can be conveniently switched between "on" and "off" states by using the external magnetic field, as shown in the schematic illustrations and optical microscopy images in Figure 1c. In a vertical field, the particle chains stand straight so that their diffraction is turned "on" and the corresponding color can be observed from the top. Each bright green dot in the optical microscopy image actually represents one vertically aligned particle chain. On the contrary, when the field is switched horizontally, the microspheres are forced to rotate 90° to lay down the particle chains so that the diffraction is turned off and microspheres show the native brown color of iron oxide. Interestingly, the particle chains can be directly observed by careful inspection of the microspheres through optical microscopy. The rotation of microspheres is instant and synchronized with the manual movement of external fields, as supported by the videos in the Supporting Information.

Depending on the direction of the external magnetic field, the particle chains may be suspended at any intermediate stage between the on and off states with a specific tilting angle (θ). We have investigated the dependence of diffraction peak wavelength (λ) and intensity on the tilting angle (θ) using an optical microscope coupled with a spectrometer (Figure 2). While the magnetic field is tuned within the plane constructed by the incident light and back scattered light, the diffraction from an isolated microsphere is recorded correspondingly by

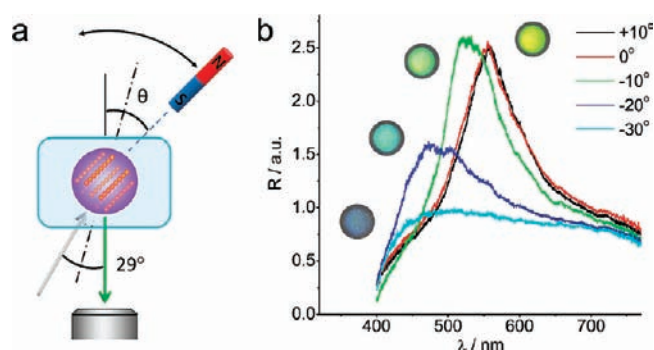


Figure 2. (a) Schematic illustrations of the experimental setup for studying the angular dependence of the diffraction property of the magneto-chromic microspheres. (b) Reflection spectrum and corresponding digital photo recorded from a single $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ microsphere at different tilting angles.

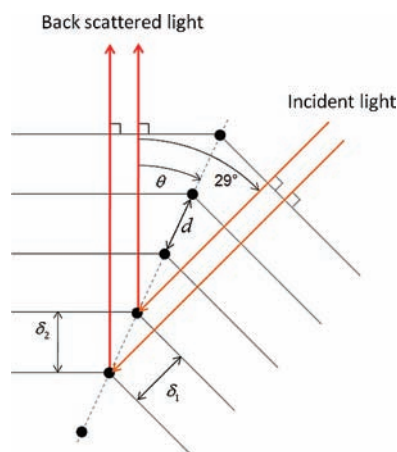


Figure 3. Schematic illustration of geometric relation of incident light, back scattered light, and chain-like photonic structures for the simulation of diffraction wavelength at different tilting angles.

the spectrometer, as schematically shown in Figure 2a. It has been found that the diffraction peak blue shifts with decreasing intensity when the magnetic field direction is manipulated away from the angular bisector of incident light and back scattered light ($\theta \approx 14.5^\circ$). Figure 2b shows the spectra and corresponding microscopy images when the angle θ is tilted from $+10^\circ$ to -30° . Such a change in the diffraction peak position and intensity closely resembles the characteristics of a one-dimensional Bragg photonic crystal, as proven by the close match between the experimental results and theoretical simulations.

The dependence of diffraction wavelength (λ) upon magnetic field tilting angle (θ) was simulated by formula ($\lambda = nd[\cos(29^\circ - \theta) + \cos \theta]$) using MatLab. The refractive index (n) of PEGDA is 1.46, and the interparticle spacing within the chains is calculated to be 200 nm using the diffraction wavelength at $\theta = 0^\circ$. We consider the chain-like structure as an ideal one-dimensional photonic crystal composed of dots with negligible volume. According to the physical model in Figure 3, the optical path difference (δ) and phase difference (ϕ) can be expressed by eqs 1 and 2. Then, total amplitude (A) and intensity of back scattered light can be calculated by eqs 3 and 4. Since the maximum back scattering condition is only achieved as the phase difference satisfying the eq 5, the final expression of diffraction wavelength will be deduced as eq 6.

$$\delta = \delta_1 + \delta_2 = nd \cos(29^\circ - \theta) + nd \cos \theta \quad (1)$$

$$\phi = \phi_1 + \phi_2 = \frac{2\pi}{\lambda} \delta \quad (2)$$

$$\begin{aligned} A &= f + fe^{i\phi} + fe^{i2\phi} + \dots + fe^{in\phi} + \dots \\ &= f \sum (1 + e^{i\phi} + e^{i2\phi} + \dots + e^{in\phi} + \dots) = f \frac{1}{1 - e^{i\phi}} \end{aligned} \quad (3)$$

$$\begin{aligned} |A|^2 &= AA^* = f^2 \left(\frac{1}{1 - e^{i\phi}} \right) \left(\frac{1}{1 - e^{-i\phi}} \right) = \frac{f^2}{2 - (e^{i\phi} + e^{-i\phi})} \\ &= \frac{f^2}{2(1 - \cos\phi)} \end{aligned} \quad (4)$$

$$\phi = \frac{2\pi}{\lambda} \delta = 2m\pi \quad (5)$$

$$\lambda = \delta = nd[\cos(29^\circ - \theta) + \cos \theta] \quad (6)$$

The simulated results are compared with the experimental data in Figure 4, both of which indicate that the diffraction peak wavelength has a maximum value when the particle chain is tilted along the angular bisector of incident light and back scattered light ($\theta \approx 14.5^\circ$). When the tilting angle is manipulated away from 14.5° to $+20^\circ$ to $+50^\circ$ or decrease from $+10^\circ$ to -30° , the diffraction peak blue-shifts and its intensity gradually decreases. This behavior is consistent with the typical characteristics of one-dimensional Bragg photonic crystal. Beyond -30° or $+50^\circ$, the diffraction intensity is very low so that the photonic state of the microsphere can be practically considered as “off”. Figure 5 demonstrates the complete on/off switching of magneto-chromic microspheres that originally diffract blue, green, and red light. These microspheres are synthesized by starting with SPM particles with average diameters of 127, 154, and 197 nm. It is believed that a simple mixing of RGB microspheres with various ratios would produce a great number of colors that can be collectively perceived by human eyes.

The average size of the microspheres can be easily controlled using the simple dispersing process through the choices of the oil type and the speed of mechanical stirring. No significant efforts have been made in this paper to optimize the size distribution of the droplets as our focus is on the creation and photonic property of the microspheres, although many interesting methods including those using microfluidic devices are available to produce monodispersed microdroplets.^{39–43} In general, using high speed stirring and viscous oils leads to the formation of smaller emulsion droplets. The microspheres prepared in mineral oils have average diameters above $50 \mu\text{m}$, and those prepared in silicone oils have average diameters less than $30 \mu\text{m}$. Figure 6a shows a series of dark-field optical microscopy images of differently sized microspheres selected from the samples made by using the same $\text{Fe}_3\text{O}_4/\text{PEGDA}$ mixture but with either mineral oil or silicone oil as the

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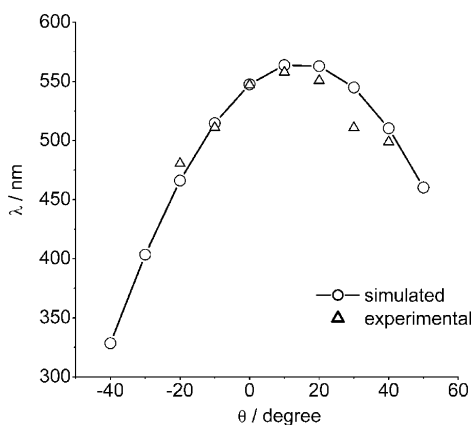


Figure 4. Simulation and experimental data showing the dependence of diffraction wavelength (λ) of a single $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ microsphere on the magnetic field tilting angle.

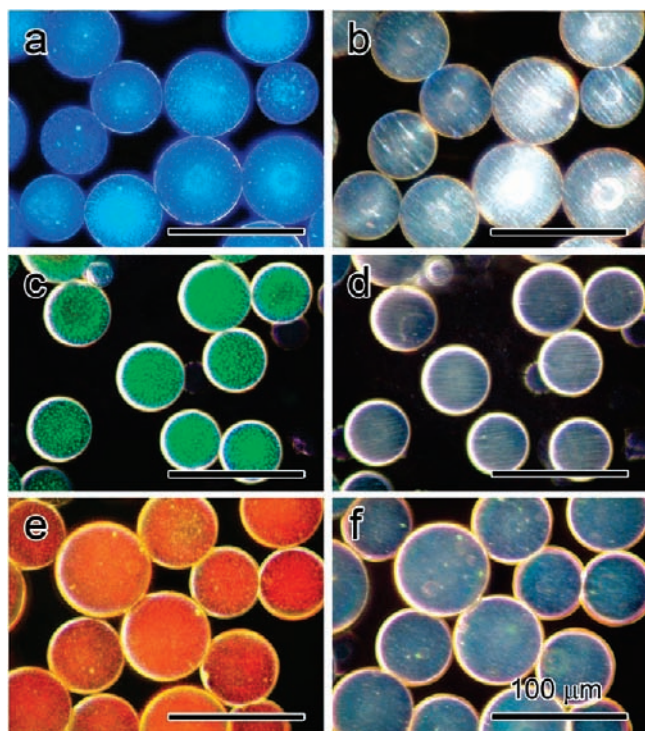


Figure 5. Optical microscopy images ($500\times$) of magnetochromatic microspheres with diffractions switched between “on” (a, c, e) and “off” (b, d, f) states by using external magnetic fields. These microspheres are prepared using (a, b) 127, (c, d) 154, and (e, f) 197 nm $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ colloids.

continuous phase. Vertical external fields are applied so that these microspheres are all at the “on” state. Microspheres larger than $10\ \mu\text{m}$ containing particle chains with spacing such that they reflect red light all display the expected red color, which comes from the diffraction of many vertically aligned particle chains. Bright red dots, which contribute to the overall production of red color, can be clearly observed inside the microspheres when they are imaged at higher magnification. However, in the case of microspheres $10\ \mu\text{m}$ and smaller containing similarly spaced particle chains, fewer red dots can be observed in the center. Instead, contribution of the diffraction from the edge to the overall color of the microspheres gradually increases, with a progressive blue shift from orange to yellow and eventually

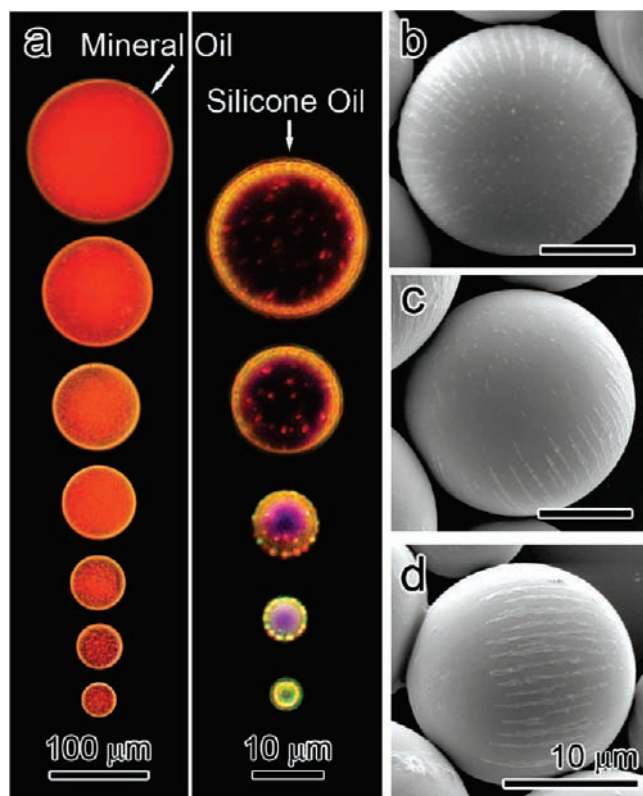


Figure 6. (a) Dark-field optical microscopy images of a series of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ microspheres with diameters from ~ 150 to $4\ \mu\text{m}$. The larger microspheres were fabricated in mineral oil, and smaller ones in silicon oil. (b–d) Top view to side view SEM images of the microspheres, showing some of the $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ particle chains aligned on the surface along the longitudinal direction. Note that many particle chains are embedded inside the microspheres, with only ends occasionally observable in the top view image (b).

yellow-green as the microsphere size is reduced. This phenomenon can be explained by the unique self-assembly behavior of SPM particles in the PEGDA droplets. Figure 6b–d show the top-view and side-view SEM images of the typical microspheres, suggesting that the SPM particle chains are not only embedded inside the microspheres in the form of straight strings but also laid on the curved surface along the longitudinal direction. The “bent” assembly of SPM particles on the microsphere surface can be attributed to the combined effect of the spherical confinement of the emulsion droplets and the magnetically induced strong repulsive force perpendicular to the direction of the external field. The bent surface assemblies can be viewed as chains tilted from the vertical direction with the degree of tilting determined by the curvature of the microspheres. As the microspheres become smaller, the curvature becomes larger and the tilting angle increases, leading to a blue shift of the diffraction. Additionally, the higher surface to volume ratio of smaller microspheres may also increase the ratio of surface chains to embedded ones and eventually change the overall diffracted color of the spheres. For microspheres larger than $10\ \mu\text{m}$, the embedded straight assemblies dominate and the bending of the surface assemblies is small, so that the microspheres show uniform colors.

The optical response of the microspheres to the external magnetic field was characterized by the switching threshold of field strength and switching frequency, which describe how strong of an external magnetic field is required to rotate the microspheres and how fast the microspheres respond to the

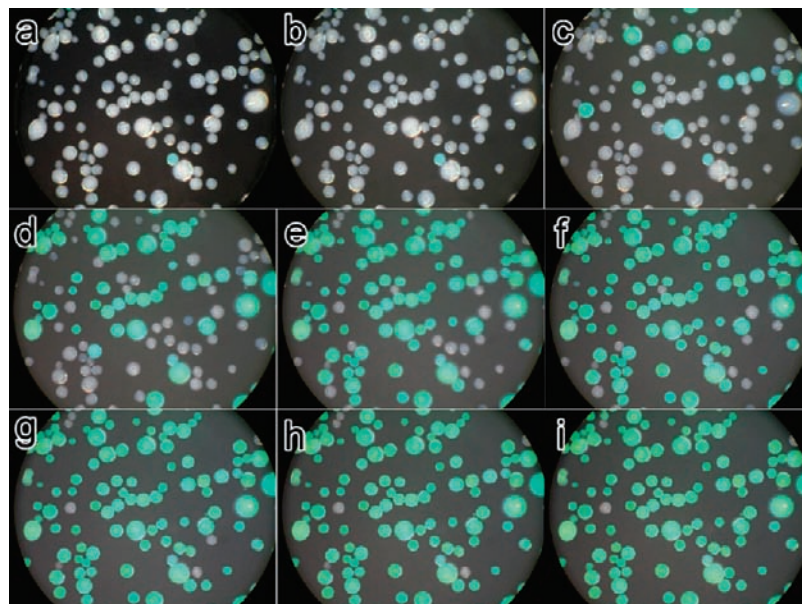


Figure 7. Measurement of turning threshold by analyzing the optical microscopy images of magnetochromatic microspheres in an increasing magnetic field from (a) 20 G to (i) 340 G with a step of 40 G.

changes in the magnetic field, respectively. First, a low concentration of microspheres dispersed in a density matched solvent—PEGDA liquid were used to measure the switching threshold. The dispersion was sandwiched between two hydrophobic glass slides to avoid adhesion to the glass substrate. With increasing magnetic field strength, the microspheres were gradually turned “on” (Figure 7), and digital photos were taken after ~ 5 s of every change in the field strength. Figure 8 shows the statistic diagrams of the percentage of microspheres (counted in viewable area) that have been turned “on” in an increasing field for two samples with different loading of the magnetic materials. The corresponding accumulative curves are also plotted from the diagrams. It has been found that the loading of the magnetic materials in the microspheres but not the sphere size is the key factor which determines the switching threshold of field strength. For microspheres with low magnetic loading (8 mg $\text{Fe}_3\text{O}_4/\text{mL}$ PEGDA), 80% of them can be turned on in a magnetic field of 180 G, while, for microspheres containing more SPM particles (16 mg $\text{Fe}_3\text{O}_4/\text{mL}$ PEGDA), only a 100 G magnetic field is required to turn on the same number of spheres.

The switching of diffraction could be accomplished rapidly (< 1 s) in a sufficiently strong magnetic field. The turning frequency of the microspheres was measured with a test platform built with a halogen light source, a spectrometer, and a rotating magnet unit with a geared DC motor as shown in Figure S6. The rotating plate with NS and SN magnets standing alternately will produce a periodical vertical (1100–1200 G) and horizontal magnetic field (300–400 G), whose frequency can be simply controlled by the rotating speed of the plate. Figure 9 shows the diffraction of microspheres in a 1.22 and 3.33 Hz vertical/horizontal alternating magnetic field, demonstrating that the photonic microspheres can be rotated quickly. It is noted that the rotating amplitude gradually decreases with the increase of turning frequency, primarily due to the relatively weak horizontal field strength. When the frequency is higher than 7 Hz (Figure S7), the rotation of microspheres cannot catch up with the external field variation so that they seem to simply vibrate around the vertical state and the diffraction remains on all the time. The switching frequency might be further improved when

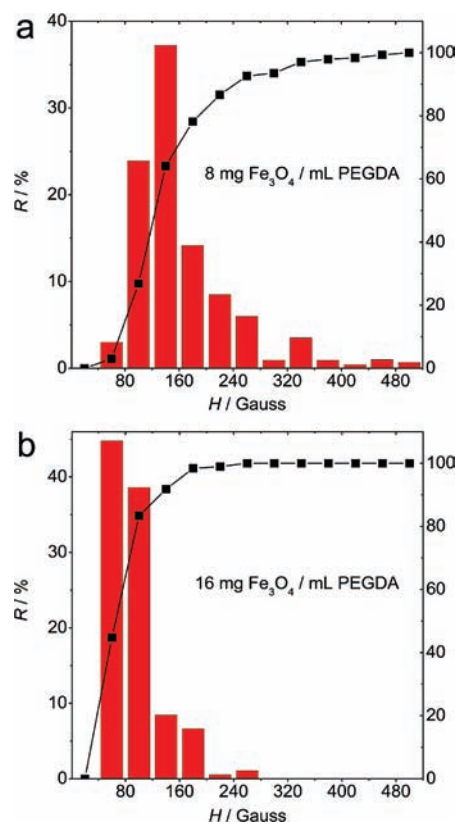


Figure 8. Turning threshold of field strength for $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{PEGDA}$ microspheres with different loadings of magnetic particles: (a) 8 and (b) 16 mg $\text{Fe}_3\text{O}_4/\text{mL}$ PEGDA. Statistical diagrams show the percentage of viewable area which is turned on at certain field strengths. The corresponding accumulative curves are also provided.

the microspheres are dispersed in a less viscous solvent or tuned in magnetic fields with higher strengths.

Incorporation of photonic crystals into microspheres allows tuning of the photonic property by simply controlling the sphere orientation, making it very convenient to create bistable states that are required for many applications such as displays. Here

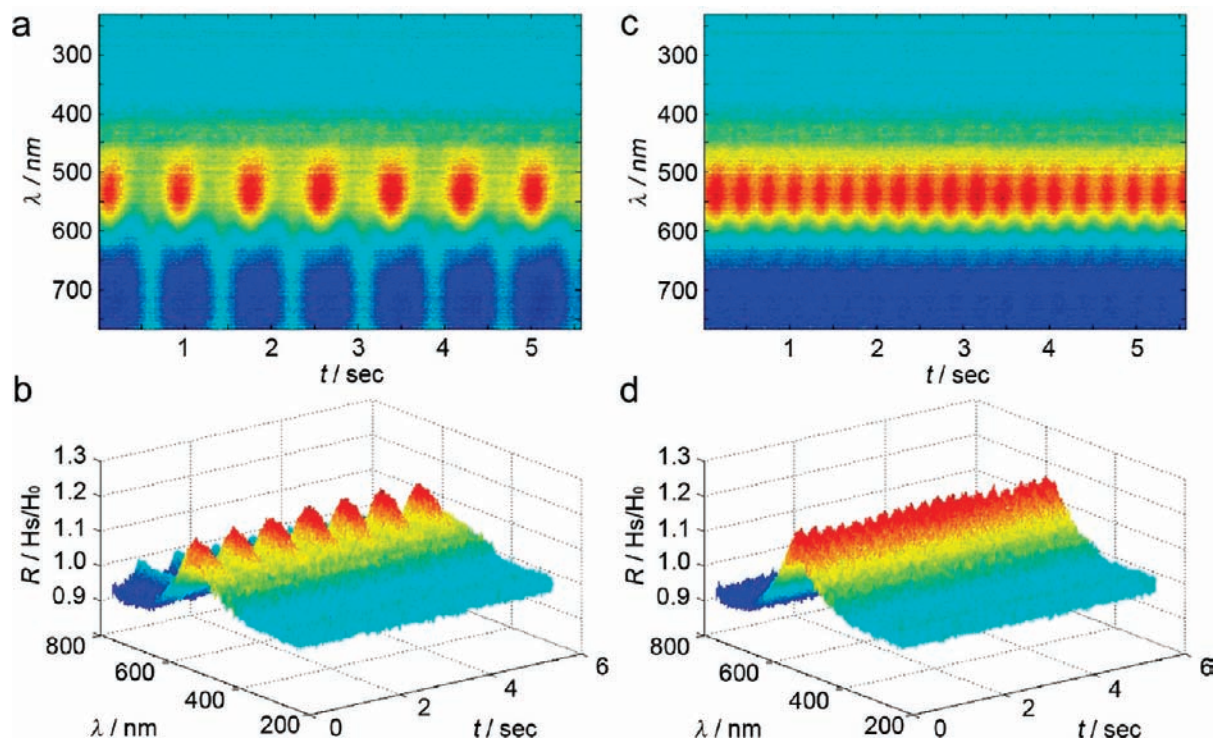


Figure 9. Optical response of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ microspheres in a (a, b) 1.22 and (c, d) 3.33 Hz vertical/horizontal alternating magnetic field. H_s/H_0 is the ratio of reflection with H field to that without H field.

we demonstrate a simple switchable color display system in which the color information can be rewritten multiple times by means of a magnetic field. The basic idea is to create bistable states by embedding the microspheres into a matrix that can be switched between liquid and solid states. Many long chain hydrocarbons and short chain polymers, such as paraffin and poly(ethylene glycol), have melting points slightly above room temperature. When heated, the matrix material melts, allowing the display of colors by aligning the microspheres using magnetic fields. When the system is cooled to room temperature, the matrix solidifies and the orientation of microspheres is frozen so that the color information remains for a long time without the need of additional energy. An external magnetic field cannot alter their color once the orientation of microspheres is fixed by the matrix. Reheating the matrix materials, however, will erase the particular color by randomizing the orientation of the microspheres or by magnetically reorienting the microspheres to a completely “off” state. Figure 10 shows three examples of such displays fabricated by embedding the microspheres in PEG ($M_w = 1500$) films which can be melted at $\sim 46^\circ\text{C}$. The comparison of digital photos and reflection spectra clearly demonstrates two stable diffractive states at room temperature, suggesting the possible applications of such systems as economical and rewriteable color display units.

Conclusion

Magnetochromatic microspheres have been prepared through a simultaneous magnetic assembly and UV curing process in an emulsion system. Superparamagnetic $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ colloidal particles are self-organized into ordered structures inside emulsion droplets of UV curable resin, followed by an immediate UV curing process to polymerize the droplets and fix the ordered structures. By rotating the microspheres, it is very convenient to control the orientation of the magnetic chains and thereby

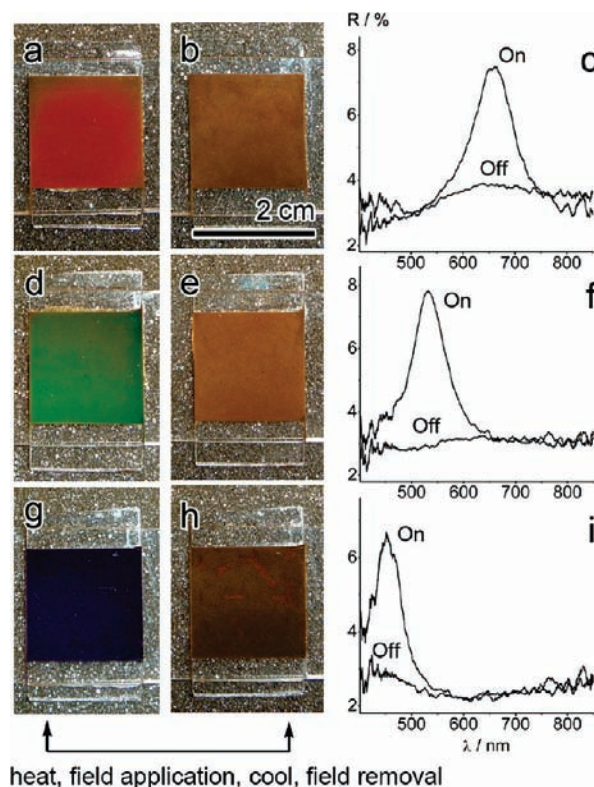


Figure 10. Digital photos and reflection spectra of three types of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PEGDA}$ microspheres loaded in $1.8 \times 1.8 \times 0.1 \text{ cm}^3$ glass cells filled with PEG ($M_w = 1500$). The diffraction is switched on (a, d, g) or off (b, e, h) by melting the PEG matrix, rotating the microspheres with a magnetic field, and finally cooling down the PEG matrix to lock the sphere orientation. Bistable states can therefore be maintained in the absence of magnetic fields. The corresponding reflection spectra (c, f, i) display diffraction peaks at the “on” stage and none at the “off” stage.

the diffractive colors using external magnetic fields. Many copies of microspheres can be produced using the simple process and can be tuned by external fields to collectively display uniform colors. The excellent stability, good compatibility with dispersion media, and the capability of fast on/off switching of the diffraction by magnetic fields make the system suitable for applications such as color display, signage, bio- and chemical detection, and magnetic field sensing.

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Supporting Information Available: Experimental setup, low magnification optical microscope images and SEM images of microspheres, TEM images and size distribution of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ colloids, spacial profile of magnetic field strength, optical response in higher frequency magnetic field. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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