DOI: 10.1002/anie.200701992

Highly Tunable Superparamagnetic Colloidal Photonic Crystals**

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Colloidal crystals, periodic structures typically self-assembled from monodisperse colloidal building blocks, are one class of photonic band gap materials that can be fabricated at low cost and on a large scale.[1–3] They have attracted much attention because of their promise in optoelectronic applications that require the manipulation of photons, for example, as photonic components in telecommunication devices, lasers, and sensors.[4–13] It is highly desirable for the envisioned applications that a photonic crystal possesses a tunable stop band that can be conveniently controlled by external stimuli. Considerable effort has been devoted to achieving this goal by changing the refractive indices of the materials and the lattice constants or spatial symmetry of the crystals through the application of chemical stimuli, mechanical forces, electrical fields, or light.[14–23] However, the wide use of these systems as optoelectronic devices is hampered by the limited tunability of the stop band (changes in peak position are typically in the range of tens of nanometers), the slow response to the external stimuli, and the difficulty of integration into existing photonic systems.

Adding magnetic components to the colloidal building blocks provides an opportunity for convenient and precise control of the properties of photonic crystals through an external magnetic field. Asher and co-workers explored this approach by fabricating colloidal photonic crystals using highly charged polystyrene microspheres containing superparamagnetic nanoparticles.[24,25] In this case, the magnetic forces exerted on the colloids are weak relative to interparticle electrostatic forces because of the low loading of the magnetic materials, leading to a limited tuning range, a long response time, and consequently limited practical applications. Preparation of polymer microspheres with increased loading of magnetic materials is practically difficult within the typically used emulsion polymerization schemes. In principle, colloidal particles of pure magnetic materials such as iron oxide can be directly used as the building blocks for constructing colloidal photonic crystals. Such effort, however, is limited by the superparamagnetic-to-ferromagnetic transition that occurs as particles are grown into larger domains.[26] Recently, we developed a method for the preparation of polyacrylate-capped superparamagnetic magnetite (Fe_3O_4) colloidal nanocrystal clusters (CNCs) with tunable sizes from 30 to 180 nm by a high-temperature hydrolysis process.[27] Each cluster is composed of many magnetite crystallites of approximately 10 nm, thus retaining the superparamagnetic properties at room temperature. Herein, we report that such superparamagnetic clusters can be directly employed for constructing colloidal photonic crystals with highly tunable stop bands that can be moved across the entire visible spectral region owing to the highly charged polyacrylate-capped surfaces and the strong interaction of the magnetite CNCs with a magnetic field. Our approach employs simple and inexpensive synthetic methods and yields photonic crystals with wide and reversible tunability, and an instant response to external magnetic fields; as such, it could lead to many critical applications that would not otherwise be accessible.

Uniform magnetite CNC building blocks were synthesized by hydrolyzing $FeCl_3$ with the addition of NaOH at around 220 °C in a solution containing polyacrylic acid (PAA) as a surfactant in diethylene glycol (DEG).[27] After they are cleaned, the CNCs can be dispersed in water and remain stable in solution for at least several months. A representative TEM image of magnetite CNCs (Figure 1 a) shows that the monodisperse colloids consist of small primary particles. As schematically illustrated in Figure 1 b, polyacrylate binds to the particle surface through the strong coordination of carboxylate groups with iron cations, whereas the noncoordinated carboxylate groups on the polymer chains extend into aqueous solution and render the particle surfaces highly charged. Since each of them is composed of small primary nanocrystals, the CNCs retain the superparamagnetic behavior at room temperature and show much higher saturation magnetization than individual nanodots. Figure 1 c shows the hysteresis loop of a sample of 180-nm CNCs measured at room temperature which display superparamagnetism.

After the extra surfactants are removed and the ionic strength is decreased through repeated cleaning by centrifugation, the Fe_3O_4 CNCs readily self-assemble in deionized water into colloidal crystals upon application of a magnetic field. Figure 1 d,e shows the photos and reflection spectra of an aqueous solution of 120-nm CNCs (ca. 8.6 mg mL^{-1}) in response to a varying magnetic field achieved by controlling the distance between a NdFeB magnet and the sample. The peak resulting from the diffraction of (111) planes blue-shifts from 730 to below 450 nm as the magnetic field increases from 87.8 to 352 G by moving the magnet towards the sample (3.7–2.0 cm). As explored in detail below, a rapid shift (< 1 s) of the stop band is observed in response to the change in the strength of magnetic field. The interplanar spacing decreases from 274 to 169 nm as the strength of magnetic field increases,

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[**] Y.Y. thanks the University of California, Riverside, for start-up funds and Dr. C. K. Erdonmez for helpful discussions. We thank Prof. W. P. Beyermann and Dr. M. Biasini for help with magnetic-property measurements and Dr. Bozhilov and Mr. McDaniel at the Central Facility for Advanced Microscopy and Microanalysis at UCR for assistance with TEM analysis.

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as estimated by Bragg's Law ($\lambda = 2nd\sin\theta$; λ is the diffraction wavelength, n is the refractive index of water, d is the lattice plane spacing, and $\theta = 90°$ is the Bragg angle).[25]

The tuning range of the diffraction wavelength is related to the average size of the CNCs. In general, crystals of large clusters (160–180 nm) preferentially diffract red light in a relatively weak magnetic field, and their ordered structures become unstable when the magnetic field is too strong. Small clusters (60–100 nm) form ordered structures only when the magnetic field is sufficiently strong and the crystals preferentially diffract blue light. As demonstrated by the example in Figure 1, medium-size clusters can form stable colloidal crystals in a magnetic field with tunable stop bands covering the whole visible spectrum. This size dependence is clearly shown in Figure 2, which plots the tuning range and the peak position against the average size of the clusters. For each sample, the position of maximum diffraction intensity is determined by polynomial fitting of the curve consisting of all peak values of the reflection spectra, and the tuning range is obtained by including all the diffraction peaks whose intensity is above 30 % of the maximum value. Figure 2 indicates that the diffraction peak with maximum intensity red-shifts as the size increases approximately in a linear fashion, which agrees with our qualitative observations.

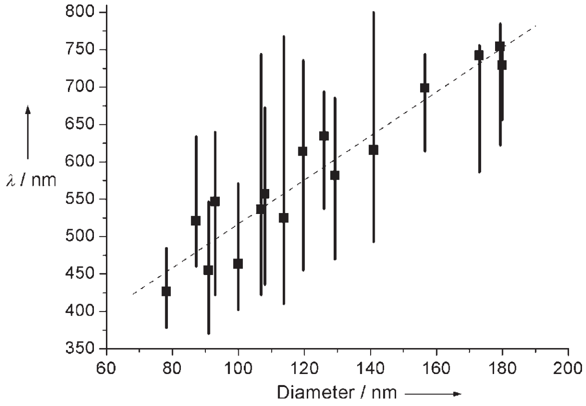

Figure 2. Size dependence of the tuning range (vertical bars) and the wavelength of maximum diffraction intensity (solid squares). The tuning range is defined as the range of wavelengths of the diffraction peaks whose intensity remains above 30 % of the maximum value achieved by varying the applied field.

The optical response of the colloidal photonic crystals to the changes in external magnetic field is fully reversible. Figure 3 a shows the blue shift of the diffraction peak of a

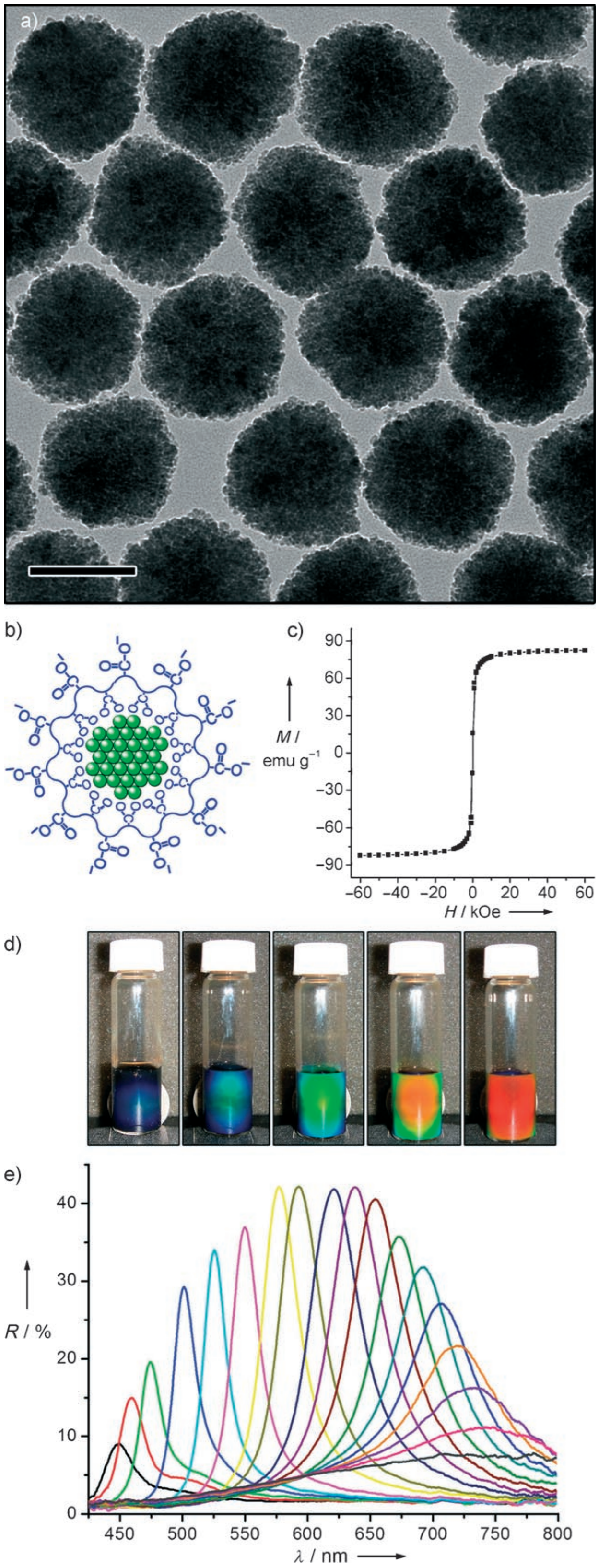

Figure 1. a) TEM image and b) schematic illustration of polyacrylate-capped Fe_3O_4 colloidal nanocrystal clusters. Scale bar: 100 nm. c) Hysteresis loop of 180-nm CNCs measured at room temperature exhibiting superparamagnetic behavior. d) Photographs of colloidal crystals formed in response to an external magnetic field; the magnet–sample distance decreases gradually from right to left. e) Dependence of the reflection spectra at normal incidence of the colloidal crystals on the distance of the sample from the magnet. Diffraction peaks blue-shift (from right to left) as the distance decreases from 3.7 to 2.0 cm with step size of 0.1 cm. The average diameter of the CNCs in this sample is 120 nm.

solution of 93-nm CNCs in response to an increasing magnetic field induced by reducing the distance between the magnet and the sample. The reverse process by moving the magnet away from the sample red-shifts the diffraction peak back to the original position (Figure 3b). The peak positions show little hysteresis in that most of them are close for a given magnet–sample distance in either the forward or reverse direction of motion of the magnet. The slight mismatches observed for a few points might be due to inaccurate manual placement of the magnet, as small errors in distance will alter the magnetic field strength felt by the colloidal sample (see the Supporting Information). The colloidal crystals are very stable and no precipitation of the CNCs was observed during the experiment.

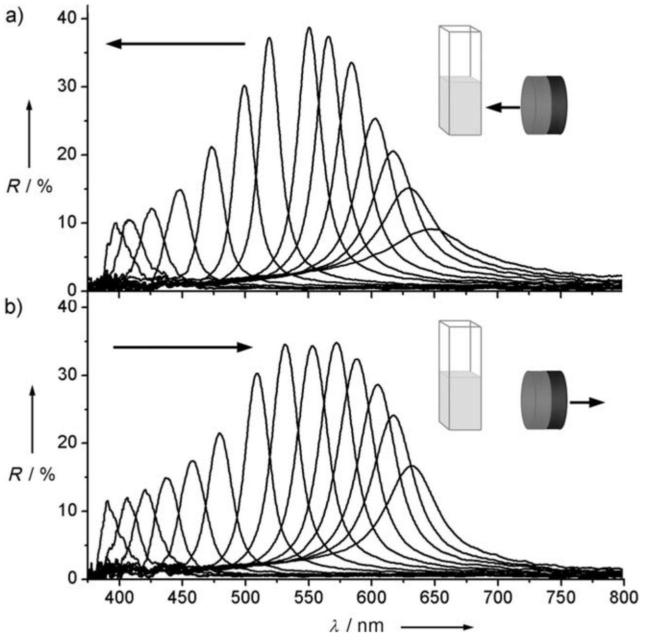

Figure 3. Reversible optical responses of 93-nm Fe_3O_4 colloidal photonic crystals to varying external magnetic field. Diffraction peaks blue-shift (a) as the magnet–sample distance decreases from 3.1 to 1.8 cm, and red shift (b) as the distance increases from 1.8 to 3.1 cm in step sizes of 0.1 cm in both cases.

The Fe_3O_4 colloidal photonic crystals have a fast optical response to the external magnetic field, which is a critical feature for some practical applications. To characterize the response time, we recorded changes in the reflection spectrum of a magnetic colloidal photonic crystal in the presence of a periodically switched magnetic field with a controllable switching frequency. Figure 4a shows the reflection spectra of a "blue" photonic crystal in a 0.5-Hz periodic magnetic field, demonstrating that the diffraction at around 470 nm is switched on and off at the same frequency as the external field. While keeping all the other parameters the same, we recorded the variation of peak intensity at 470 nm in response to electromagnetic fields at higher frequencies, such as 1 and 2 Hz. The diffraction intensity shows periodic modulations which closely match the profile of external field (Figure 4b,c), displaying clear on and off states with the corresponding frequency. No gradual transition from longer wavelengths to the final shorter wavelength was observed during the development of the spectra, indicating that the ordered structures form within the first 200 ms after application of the magnetic field. During the rest of the "on" stage, the order of the crystals further improves as the remaining particles rearrange their positions, as indicated by the gradual increase in the diffraction intensity. This result also explains why the diffraction intensity is relatively lower at higher frequencies. The diffraction peak disappears completely within 100–200 ms after the magnetic field is switched off, which is much faster than the time needed for development of translational order under a magnetic field.

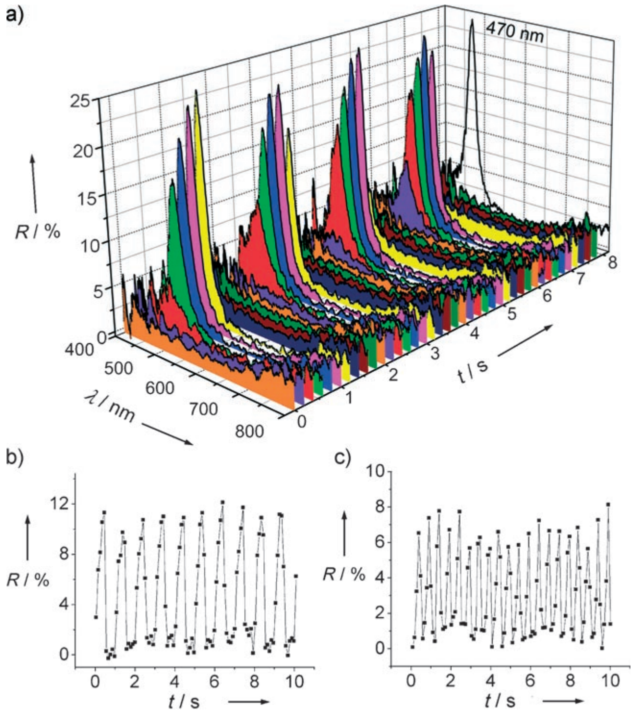

Figure 4. a) Modulated optical responses of 70-nm Fe_3O_4 colloidal photonic crystals in a 0.5-Hz periodic magnetic field (spectra integration time 200 ms). b, c) Variation of diffraction peak intensity at 470 nm in response to a 1-Hz (b) and 2-Hz (c) periodic magnetic field (spectra integration time 100 ms).

The three-dimensional order of the formed colloidal crystals is the balanced result of the interparticle electrostatic repulsive force and the magnetic forces.[24,25] As-synthesized CNCs before cleaning show no color change even when the magnetic field is so strong that they are separated from the solution. Their optical response to the magnetic field increases with the number of cleaning cycles, which reduce the ionic strength of the solution and increase the Debye–Hückel screening length and therefore the electrostatic repulsion.[28] In contrast, the addition of electrolyte significantly reduces the screening length and leads to a blue shift of the reflection peaks and reduction of reflection intensity. ξ-potential measurement of a sample cleaned five times gave a typical value of −51 mV, demonstrating its highly charged surface.

As CNCs are composed of pure Fe_3O_4, the magnetic forces they experience in a magnetic field are so strong that they are comparable to the electrostatic interactions. As reported previously, the application of a magnetic field to superparamagnetic colloids in solution results in additional magnetic packing forces, as well as magnetic dipole–dipole repulsive and attractive forces.[25] The magnetic packing force is exerted on every cluster and attracts them towards the maximum of the local magnetic gradient. The repulsive and attractive forces are perpendicular and parallel to the magnetic field, respectively. For example, a 120-nm cluster shows a magnetic moment μ of about 6.3×10^{-14} emu in a magnetic field of 235 G and experiences a magnetic packing force ($\boldsymbol{F}_\mathrm{m} = \bigtriangledown(\mu\boldsymbol{B})$; $\boldsymbol{B}$ = magnetic induction) of 1.3×10^{-11} dyn in a gradient of $200\,\mathrm{G\,cm^{-1}}$. When the nearest-neighbor spacing d derived from the diffraction peak position is 197.4 nm, the interparticle repulsive force $\boldsymbol{F}_\mathrm{mr} = 3(\mu^2/d^4)$ and the attractive force $\boldsymbol{F}_\mathrm{ma} = 6(\mu^2/d^4)$ are estimated to be 7.9×10^{-8} and 1.6×10^{-7} dyn, respectively. These values are about 20 times higher than those of polymer beads loaded with iron oxide nanocrystals under similar conditions, and they are comparable to that of the interparticle electrostatic repulsive force. The magnetic attractive force is believed to be the major force to bring the particles together, as evidenced by the fact that no crystallization can occur if the original interparticle distance is too large, for example, when the current particle concentration is decreased by a factor of 10. We believe that the broad tunability and rapid responses of the current system benefit from the large contribution of the magnetic forces in determining the structure and dimension of the lattices.

In summary, colloidal photonic crystals with magnetically tunable stop bands covering the entire visible spectrum have been fabricated from superparamagnetic magnetite CNCs. The optical response of these photonic crystals to external magnetic stimuli is rapid and fully reversible. It is believed that such field-responsive photonic materials will provide a new platform for the fabrication of novel optical microelectromechanical systems, sensors, and color display units.[29]

Received: May 4, 2007

Keywords: colloids · magnetic properties · nanostructures · photonic crystals

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