Magnetically responsive colloidal photonic crystals

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Magnetically responsive colloidal photonic crystals have been fabricated by using highly charged superparamagnetic Fe_3O_4 colloidal nanocrystal clusters (CNCs) as the building blocks. The colloids form chainlike structures with regular interparticle spacing of a few hundred nanometers along the external field so that the system strongly diffracts light. The diffraction wavelength can be tuned across the entire visible spectrum by simply changing the strength of the magnetic field. The fast and reversible response suggests great potential of these photonic materials in applications such as displays and sensors. Further modification of the Fe_3O_4 CNCs with silica coating allows the dispersion of the particles in nonaqueous solutions. The modified particles also self-assemble into ordered structures in alcohol solvents under an external magnetic field. Embedding droplets of such a colloidal solution in a polymer matrix produces solid composite materials with magnetically responsive optical properties.

Functional photonic materials and devices can be created by assembling monodisperse colloidal particles into periodically ordered structures.[1–9] Stimulated by the important applications in optical switches and interconnects, sensors, and displays, considerable effort has been devoted to the development of tunable photonic crystals whose properties can be controlled by external stimuli. In principle, the stimuli can be any chemical and physical means that can effectively cause changes in the refractive indices of the colloids or the surrounding matrix, the lattice constants and symmetry of the colloidal arrays. Typically, these stimuli include temperature, mechanical force, electrical or magnetic field, light, or changes in pH and ionic strength of the system.[10–22]

An effective means for controlling the lattice spacing and thus the photonic properties is to introducing magnetic components to the colloidal building blocks.[23] Previous work by Bibette *et al.* reported that emulsion droplets containing γ-Fe_2O_3 nanoparticles can form one-dimensional chain structures and diffract light in the visible range in the presence of an external magnetic field.[24,25] Because emulsions are not thermodynamically stable, the long-term stability of oil droplets may limit their practical applications. Asher *et al.* have developed much more stable building blocks by embedding superparamagnetic iron oxide nanoparticles into monodisperse polymer colloids through an emulsion polymerization process.[26–28] By introducing high-density charges to the colloid surface, they were able to construct three-dimensional photonic crystals by taking advantage of the strong repulsive electrostatic interactions. Field-responsive diffraction in the visible spectrum has been realized with a considerably large tuning range (~100 nm). However, the amount of magnetic components that can be introduced into the composite colloids is limited to ~17 wt% during the emulsion polymerization process. If the loading of magnetic materials in the polystyrene colloids can be significantly increased, in

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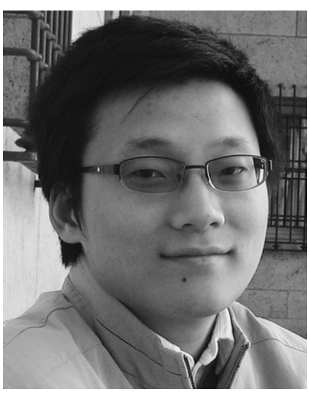

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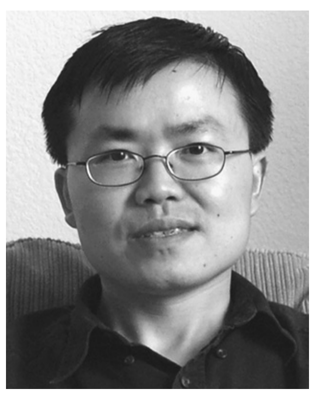

Yadong Yin

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principle, it is possible to greatly improve the system's performance including the responsive speed and the diffraction tuning range.

In fact, an ideal magnetic responsive photonic crystal can be fabricated by using colloids made of pure magnetic materials, thus favoring a faster response to the external field. Such colloids are expected to possess a uniform shape, a controllable size, and a narrow size distribution, so that the lattice constant can be precisely tuned. The particle size is preferably in the range of 100–200 nm so that the assembled structures will have periodicities comparable to the wavelength in the visible or near infrared range. Here, the superparamagnetic-to-ferromagnetic transition, which usually occurs in this size range for most ferromagnetic materials, must be avoided. Superparamagnetism is required in order to achieve a reproducible and reversible optical response because there will be no significant magnetic interactions remaining after removing the external magnetic field. The magnetic moment of each colloid has to be high enough so that strong interactions can be induced in a moderate magnetic field, ensuring a rapid photonic response. More importantly, these magnetic particles are expected to have high surface charges, thus producing sufficient repulsive force to balance the magnetically induced attractive force during assembly. The presence of both attractive and repulsive interactions with comparable strengths is believed to be the key of a successful self-assembly process.[29]

Recently, we have developed a high temperature polyol process for the synthesis of polyacrylate-capped superparamagnetic 'colloidal nanocrystal clusters' (CNCs) of magnetite (Fe_3O_4) with tunable sizes from 30 to 180 nm and relatively narrow size distributions.[30] Briefly, Fe_3O_4 CNCs are prepared by hydrolyzing $FeCl_3$ with NaOH at around 220 °C in a diethylene glycol solution with polyacrylic acid as a surfactant.[30,31] X-Ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM) studies indicate that each cluster is composed of many interconnected Fe_3O_4 nanocrystals with size of ~10 nm. Fig. 1a shows a representative TEM image of the colloidal Fe_3O_4 CNCs with an average size of ~120 nm. As schematically illustrated in Fig. 1b, polyacrylate binds to the particle surface through the strong coordination of carboxylate groups to iron cations. After repeated cleaning with water to remove the electrolyte residues, the uncoordinated polyacrylate groups render the CNC colloids highly charged on the surface and excellent water dispersibility. Because of the cluster-like structure, these CNCs still retain the superparamagnetism at room temperature.[30] Fig. 1c shows the hysteresis loop of 180 nm CNCs measured at room temperature, displaying superparamagnetism. The Fe_3O_4 CNCs also show much higher saturated magnetization than individual nanoparticles due to their greatly increased volume.[30] The combination of the relatively large size, paramagnetism, strong magnetic response, and highly charged surface makes these Fe_3O_4 CNCs the ideal building blocks for the fabrication of magnetically responsive photonic crystals.[32]

The Fe_3O_4 CNCs readily self-assemble in deionized water upon application of external magnetic field, and diffract brilliant visible light when the field strength is changed.[32] Fig. 1d and e show the photograph 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 diffraction peak shifts from 730 to 450 nm as the magnetic field increases from 87.8 to 352 Gauss. The interparticle spacing decreases from 274 to 169 nm accordingly, as estimated using 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).

The self-assembly behavior of the CNCs in response to external magnetic fields has been studied *in situ* through optical microscopy (Fig. 2).[33] A thin film of CNC solution is formed by sandwiching a CNC droplet between two cover glasses, and a vertically movable magnet is placed underneath the horizontal glasses. In the absence of a magnetic field, the colloids are well dispersed in water due to Brownian motion. When a magnetic field is vertically applied, the colloids line up along the field and appear as isolated bright spots in the optical dark field. These bright spots show short-range hexagonal order when viewed from the top (Fig. 2b). A slight tilt (~15°) of the magnet from the vertical orientation confirms that each spot is actually a chain of particles (Fig. 2c). The strong optical diffraction is therefore believed to result from the particle chains with periodical interparticle distances comparable to the wavelength of visible light.[24,25] In the plane perpendicular to the field, the short-range order and the large chain-chain separation (>2 μm) make it unlikely to diffract visible light.[33]

The ordered chain structure is determined by both electrostatic repulsion and field-induced magnetic attraction. In the absence of a magnetic field, the Fe_3O_4

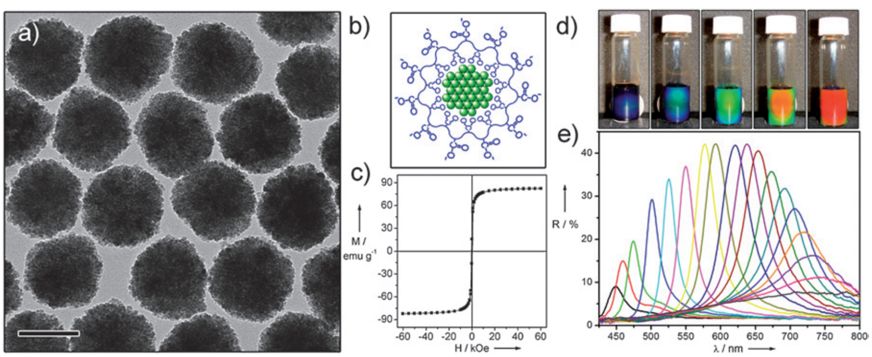

Fig. 1 a) TEM image and b) schematic illustration of polyacrylate-capped Fe_3O_4 colloidal nanocrystal clusters. Scale bar: 100 nm. c) Hysteresis loop of 180 nm CNCs measured at room temperature exhibiting superparamagnetic behavior. d) Photograph of colloidal crystals formed in response to an external 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 as the distance decreases from 3.7 to 2.0 cm with step sizes of 0.1 cm. The average diameter of the CNCs in this sample is 120 nm. Reprinted with permission from ref. 32 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

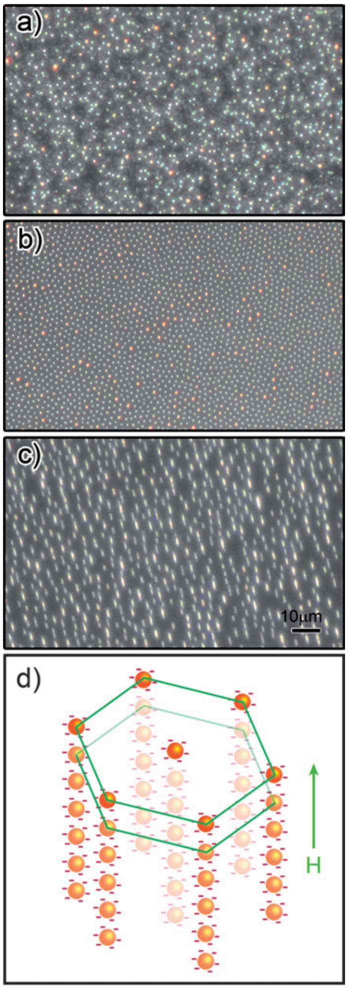

Fig. 2 (a, b) Optical microscope images showing the assembly of Fe_3O_4 CNCs dispersed in a liquid film encapsulated between two glass slides in a magnetic field parallel to the viewing angle. The field strength increases from (a) to (b). (c) Optical microscope image illustrating the assembly of CNCs into chain-like structures by slight tilting of the magnetic field (~15° from the view angle). (d) Schematic illustration of the structure of Fe_3O_4 colloids self-assembled in the presence of an external magnetic field. Adapted with permission from ref. 33 © 2008 American Chemical Society.

CNCs disperse well in water with the native brown color of iron oxide. The application of a magnetic field to the Fe_3O_4 CNC solution induces a magnetic attractive force F_{ma} between two adjacent particles along the magnetic field, therefore leading to the formation of particle chains.[34,35] As the particles get closer, the electrostatic repulsion between two highly charged colloids increases accordingly. Finally, periodic structures form in each chain as the attractive and repulsive forces between the neighboring particles reach a balanced state.[27] Because the periodicity, which determines the diffraction wavelength, is controlled by the interplay of electrostatic and magnetic forces, any means that can cause changes in these forces may be used as stimuli to tune the photonic properties of the assembled structures. A magnetic field is apparently the most convenient stimulus for this purpose because its strength can be simply controlled by varying the sample–magnet distance or electrical current if electromagnets are used. As shown in Fig. 1d and e, by moving a magnet closer to the sample, one can conveniently increase the strength of the field and therefore the induced magnetic attractive force, in turn bringing CNC particles closer together and leading to the blue shift of the diffraction peak.[32] We have also demonstrated that in a magnetic field with fixed strength, changes leading to stronger electrostatic repulsion between CNCs will increase the interparticle distance, therefore red-shifting the diffraction peak. When a stronger magnetic field is applied to balance the increased electrostatic repulsion, the colloids are organized with improved long-range order so that the diffraction intensity increases. On the other hand, a slight increase in ionic strength of the solution may significantly reduce the thickness of the electrical double layer,[36,37] thus moving diffraction peaks to shorter wavelengths.[36–38]

The range of the diffraction wavelengths that can be tuned by the external field has been found to relate to the mean size of Fe_3O_4 CNCs.[32] Generally, smaller CNCs (<100 nm) form ordered structures only under stronger magnetic fields and preferably diffract blue light. Larger clusters (>150 nm) diffract red light in a relatively weak magnetic field, and the ordered structure may become unstable when the external field is too strong. Medium-size clusters (~100–150 nm) self-assemble into stable ordered structures in both weak and strong magnetic fields, making their diffraction tunable from blue to green, yellow, and red.

The optical response of these colloidal photonic structures to the external magnetic field is fast and fully reversible. We have been able to record the switching of diffraction peaks between on and off stages at 2 Hz in an electromagnetic field operated at the same frequency. On the basis of visual observation, we believe the colloidal solution may respond to the external magnetic field at even higher frequencies. Efforts are currently being made to find the ultimate switching frequency by using high-speed spectrometers. The nucleation of an initial region with regular interparticle and interchain distances might be facilitated by the boundary conditions in a confined volume, suggesting the study of ordering kinetics in a range of confined volumes as an interesting area of research. On the other hand, the rapid switching rate of the described systems in response to external magnetic signals implies their wide potential use in telecommunication and optoelectronic devices.

Although the aqueous solution of CNCs can readily assemble into highly tunable photonic structures, some practical applications require the system operable in nonaqueous solvents. For example, the use of solvents with low volatility can significantly improve the long-term system stability and make the device fabrication process easier and more reproducible. This however becomes a challenge for polyelectrolyte-grafted CNCs because they are hardly dispersible in any nonaqueous solvents. Recently we notice that the modification of the CNC particles with a layer of silica allows their dispersion in various polar organic solvents such as methanol, ethanol and ethylene glycol (EG).[39] Interestingly, the modified particles can still self-assemble into ordered structures in these nonaqueous solvents and diffract light upon application of an external magnetic field. Considering the expected diminished contribution of electrostatic forces for silica coated particles in alcohols, it is natural to suspect that other repulsive forces must be present to counter the magnetic attractive force and yield the observed persistence of ordering. In fact, in addition to the relatively long-range electrostatic interactions, another repulsive force—"solvation force"—plays an important role in the ordering of Fe_3O_4@SiO_2 colloids in alcohol solvents.[40,41] The solvation force comes from the overlap of two solvation layers on the particle surface. A disjoining pressure develops when particles approach each other and eventually prevents them from coming even closer.[40–43] Although the electrostatic force still remains effective at larger separations, the solvation force may take over the domination of repulsions at small interparticle distances. Because the solvation force is in effect only in a very short interparticle distance and it increases dramatically for small distance changes, the diffraction peak does not blue-shift significantly when the peak intensity reaches the maximum in an increasing magnetic field. As a result, the combined effect of these two repulsive forces leads to the skewed dependence profile of the diffraction to the changes in the field strength (Fig. 3a), and reveals the "hard contact" interaction characteristics as schematically shown in Fig. 3b. In the case of highly charged Fe_3O_4 in water, the dominant repulsion force is always the electrostatic interaction. The long-range electrostatic repulsion allows the particles to assemble at a large separation distance, keeping the adjacent particles in "soft contact" with each other and displaying a symmetric profile of diffractions (Fig. 3c and d). The solvation force is also present in aqueous systems; however, its contribution to the overall repulsive interaction might be negligible because of the large interparticle distance under the operating conditions.

The formation of tunable photonic structures in nonaqueous solvents provides a number of advantages over the water-based systems for practical applications. For example, the optical response of nonaqueous systems has higher long-term stability than aqueous systems where trace amounts of ions released from environment such as glass containers may gradually alter the system's performance. Modification with a silica layer provides a convenient method for extending the diffraction wavelength beyond the visible range while maintaining the merits of the aqueous systems such as a fast and reversible response. Currently the size of Fe_3O_4 CNCs is limited to 200 nm so that the diffraction wavelength of the aqueous system is typically below ~800 nm. By coating a layer of silica with controllable thickness using the well-developed sol–gel processes,[44,45] one can easily break the size limitation and extend the diffraction of the assembled structures to the near infrared region.

Most importantly, the ability to assemble magnetic colloids in nonaqueous solvents allows us to embed such solutions into a polymer matrix in the form of liquid droplets, thus producing solid composite materials with field responsive optical properties.[39] As shown in Fig. 4a, we have successfully demonstrated such a process by firstly dispersing droplets of Fe_3O_4/EG in a liquid prepolymer of polydimethylsiloxane (PDMS) and then thermally curing the matrix. The stability of droplets is believed to benefit from the high viscosity of the PDMS prepolymer (3900 cP) and the close match of density between glycol and the PDMS matrix. Direct observation of the composite film under an optical microscope shows that the droplets, with diameter typically below 5 µm, change color in a vertically aligned magnetic field.[33] As shown in Fig. 4b, the composite film retains the flexibility of the PDMS matrix and can be folded into various shapes while still displaying magnetically induced colors. We have demonstrated a simple display unit by fabricating a patterned PDMS film which contains Fe_3O_4@SiO_2 particles with two different sizes for letters and background (Fig. 4d). Without an external field, the film shows essentially no contrast except the slight roughness at the edges of the letters. Upon the application of a magnetic field, however, blue letters with a striking contrast against the green background can be clearly observed.

In summary, magnetically responsive photonic crystals have been fabricated by assembling superparamagnetic Fe_3O_4 CNCs in water and Fe_3O_4@SiO_2 colloids in alcohol solutions. The chain structures of magnetic particles with regular

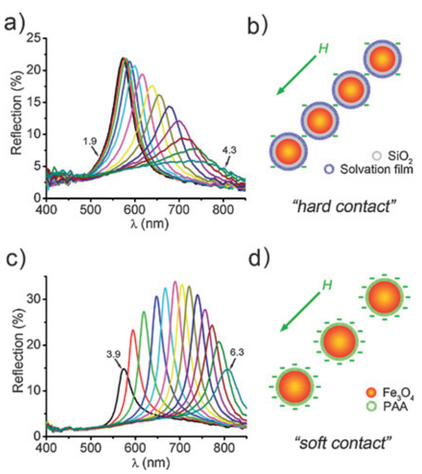

Fig. 3 (a, c) Reflection spectra of (a) 170 nm (114 nm core/28 nm shell) Fe_3O_4@SiO_2 ethanol solution and (c) 170 nm Fe_3O_4 CNC aqueous solution in response to an external magnetic field with varying strength achieved by changing the magnet–sample distance. The diffraction peak blue-shifts as the distance decreases from 4.3 to 1.9 cm for (a) and 6.3 to 3.9 cm for (c) with step sizes of 0.2 cm. (b, d) Schematic illustration and comparison of the self-assembled chain structures of (b) Fe_3O_4@SiO_2 in alcohol and (d) Fe_3O_4 CNCs in water in external magnetic fields. Adapted with permission from ref. 39 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

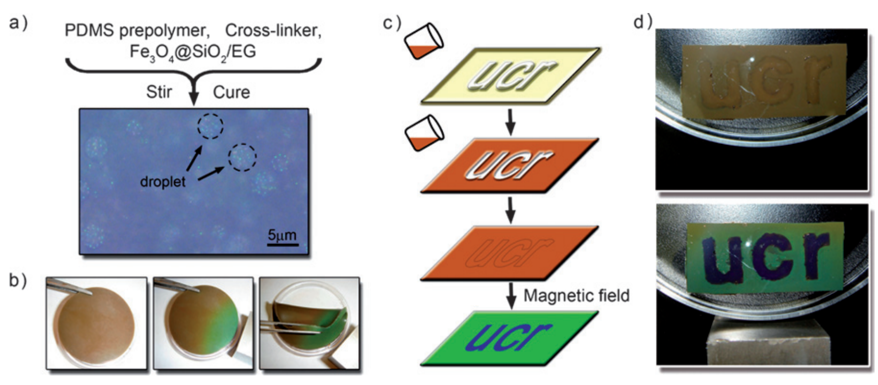

Fig. 4 (a) Fabrication procedure of a field-responsive PDMS composite embedded with droplets of EG solution of Fe_3O_4@SiO_2 colloids. The image shows an optical microscopy image of the droplets under a vertically aligned external magnetic field. The assembly of Fe_3O_4@SiO_2 colloids in the droplets under the magnetic field leads to the diffraction of green light. Each bright spot represents a chain of Fe_3O_4@SiO_2 particles assembled along the magnetic field. (b) Magnetically induced color change of a flexible PDMS film. (c) Schematic illustration of the two-step procedure for fabricating a patterned composite PDMS film which can display letters upon application of a magnetic field. (d) Digital photos of the above-mentioned patterned PDMS film. Reprinted with permission from ref. 39 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

interparticle spacings of a few hundred nanometers are formed by balancing the magnetically induced attractive force and the repulsive forces including the electrostatic force and the solvation force. The diffractions can be simply tuned by controlling the relative strength of the attractive and repulsive forces through changes in the strength of the external magnetic field, the ionic strength of the solution, and the mean size of the colloidal particles. The optical response to the external magnetic field is fast and fully reversible. The successful fabrication of field-responsive polymer composite films reveals the great potential of these optically active materials in applications such as color displays and sensors.

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