

Band-Gap-Controllable Photonic Crystals Consisting of Magnetic Nanocrystal Clusters in a Solidified Polymer Matrix

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Colloidal photonic crystals (CPhCs) consisting of iron oxide magnetic spheres possess high lattice tunability but are generally unstable and difficult to manage in liquid form. We solve the problem by introducing the colloidal spheres into a resin system, which can “freeze” three-dimensional (3D) patterns by photopolymerization. Robust solid-form CPhCs with various structural colors were, therefore, achieved. The “frozen” 3D patterns would permit not only a systematic exploration on self-assembling dynamics, colloidal crystallography, and PhC physics but also may pave a new application avenue if a solid, but still soft, PhC is shaped or sliced.

1. Introduction

The self-assembly of colloidal spheres is one of the most important approaches for producing large-volume photonic crystals (PhCs) that are working in the visible wave range.^{1–5} As the first important class of PhC prototypes, wide theoretical and experimental studies have been conducted on colloidal PhCs (CPhCs).^{2,3} Now its use has been extended from a modeling system for deep insight of PhC physics to applications, such as optical filter, decoration layers, and sensors.^{4–6} However, a vital shortcoming exists; that is, the 74% filling ratio determined by the “hard-sphere” close packing geometry is too large to attain maximal photonic band gap (PBG) effect.^{7,8} A straightforward solution to this issue is to induce particular intervals between spheres as the basic building block, as has been attempted (a) on the assembly of nanoparticles of two different materials into a binary nanoparticles superlattice⁷ and (b) by resorting to charged colloidal spheres with long-range electrostatic repulsive interactions, suspended in a liquid medium to produce order.⁸ A recent breakthrough along the second line is the work by Yin et al.,⁹ who utilized charged superparamagnetic Fe₃O₄ nanocrystal clusters to directly form CPhCs through the balance between the attractive (magnetic) force and the repulsive (electrostatic) force. The introduction of the driving force exerted by a magnetic field has led to a large tunability of the working wavelength. However, CPhCs produced this way, remaining in liquid status, are still unstable and, therefore, are difficult to manage and use. Meanwhile, those close-packed structures, including the above case (a), are fragile if the solvent is evaporated. In this paper, we solve the problem by introducing the colloidal spheres into a resin system. Taking the band-gap-controllable self-assembly of magnetic CPhCs as an example, we tune its structure to a targeted PBG featured here with a

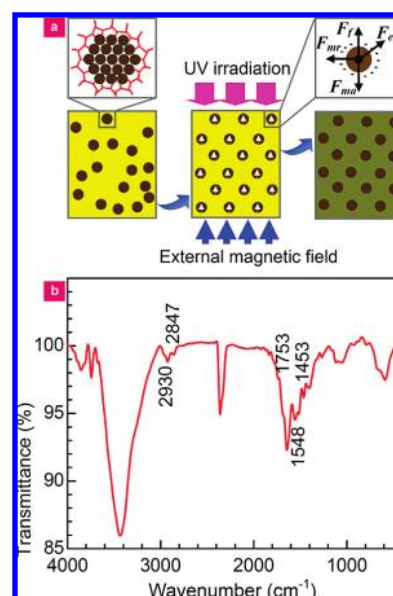


Figure 1. Synthesis, assembling, “freezing”, and the infrared characterization of Fe₃O₄ magnetic spheres. (a) An illustrative technical sequence. (b) An infrared spectrum of the PAA-capped colloidal spheres. The left-top inset represents the composition and encapsulation by PAA of a sphere, and the right-top inset illustrates the forces exerted, where their directions do not necessarily correspond to the real situation.

certain reflection wavelength and then “freeze” the 3D pattern into the solid form via photopolymerization of the matrix polymers.

2. Methods and Results

Shown in Figure 1a is the experimental scheme, where a Fe₃O₄ colloidal system was chosen for its significant lattice tunability.¹⁰ The iron spheres were produced by using a high-temperature hydrolysis reaction.^{9,10} A stock NaOH solution was prepared by dissolving 2.0 g of NaOH in 20 mL of diethylene glycol (DEG); this solution was heated at 120 °C for 1 h under

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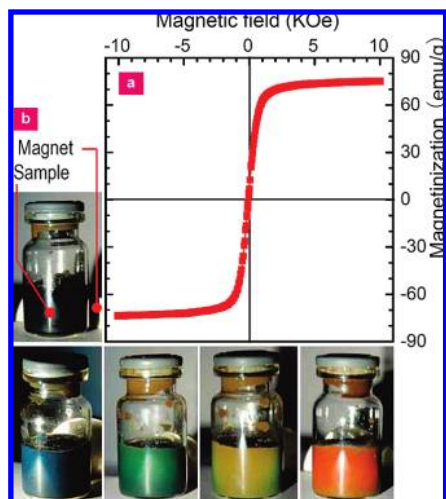


Figure 2. Magnetic performance of 142 nm sized Fe_3O_4 sphere aqueous solution. (a) A typical magnetic hysteresis loop. (b) The same solution after a magnetic field is applied. Note the black color in the left-top image, with no presence of the magnetic field.

N_2 protection and kept at 70 °C. FeCl_3 (0.8 mmol) as precursor, poly(acrylic acid) (PAA, 8 mmol) as surfactant, and DEG (34 mL, boiling point = 244–245 °C) as polar solvent were added into a three-necked flask, and the mixed solution was heated to 220 °C for 30 min under nitrogen. The NaOH solution obtained beforehand was then dropped rapidly into the mixture with vigorous mechanical stirring for an additional 1 h. The resulting black mixture was cooled to room temperature and, thereafter, washed with deionized water and ethanol three times via centrifugation. Stronger alkalinity could accelerate the hydrolysis of FeCl_3 and promote the formation of larger iron oxide spheres. As a result, Fe_3O_4 spheres of different sizes were obtained through the above procedure by adjusting the amount of NaOH solution (see Figure 3a–c; the amount of NaOH is 1.75, 1.80, and 1.85 mL, respectively). In the infrared absorption spectrum (Figure 1b), peaks located at 1753, 1548, and 1453 cm^{-1} are ascribed to the stretching of the C=O band of the carboxylic group (–COOH) and the antisymmetric and symmetric stretching of the carboxylate group (–COO–) of poly(acrylic acid) (PAA), respectively. Furthermore, the two relatively weak peaks located at 2930 and 2847 cm^{-1} are considered arising from the C–H band stretching vibration of alkane. The result indicates that Fe_3O_4 spheres are coated by PAA. Bonded at one end to the particle surface through a strong coordination of carboxylate groups with iron cations, PAA molecules render the sphere surface highly charged and water-soluble, with the other end noncoordinated carboxylate groups on the polymer chains extended into aqueous solution (Figure 1a).

The magnetic property of the spheres was examined by a vibrating sample magnetometer (VSM) (Figure 2a). The saturation magnetization reaches 71 emu/g , close to that of bulk Fe_3O_4 (92 emu/g). Here, we have to point out that the so-called Fe_3O_4 “sphere” consists actually of many magnetite crystallites with a diameter of around 10 nm.^{9,10} According to early studies, including those from us,^{9–13} the saturated magnetization of the individual crystallites is quite low so that they are difficult to be separated and dispersed in solution. The increase of the nanocrystals’ size leads to a superparamagnetic–ferromagnetic transition; in another words, Fe_3O_4 with a diameter larger than a critical size, roughly 20 nm, would lose their ability to respond to the stimuli from an external magnetic field. The formation of spheres, the nanocrystallite clusters, solved the problem. The

negligible remanence (7.7 emu/g) and coercivity (74 Oe) at 300 K estimated from the hysteresis loop (Figure 2a) exhibit clearly that the spheres made of single-crystallite aggregations retain superparamagnetic behavior at room temperature and possess higher saturation magnetization than single nanocrystals.

To further induce the iron oxide spheres into a photopolymer system,¹⁴ the precipitated particles were first dispersed into deionized water with the concentration of 8.6 mg/mL . After an ultrasonic treatment, the solution (1 mL) was mixed with a water-soluble photoresist (1 mL) in a phial (medical use) while the left portion was kept as a reference sample. The photoresist was prepared by dissolving 1-methyl-4-{2-[4-(2,2-dimethoxyethoxy) phenyl]ethenyl}quinoliniummethosulfate (164.8 mg) in 10 g of an aqueous solution that contained 15 wt % of PVA with a molecular weight of 1700 and 85% phosphoric acid (0.5 g). Under severe vibration with hands, the Fe_3O_4 sphere containing resin became homogeneous and viscous. When a magnet was drawn near the phial, both the reference (Figure 2b) and the colloidal resin (Figure 3) present a bright color, depending on the distance of the magnet: the shorter the distance is, the deeper the color becomes. The emergence of the structure colors span almost the entire visible range, a clear evidence of the formation of CPhCs, is not much affected by the difference in refractive indexes of the matrixes, 1.33 for water versus 1.36 for the polymer. However, an important difference is that almost all colors in Figure 2b were attained by distance scan the aqueous solution containing monosized iron oxide spheres, for example, 142 nm, whereas for the doped resin, more than one-sized spheres, for example, the brown mainly from 180 nm (Figure 3a), the green and yellow mainly from 155 nm (Figure 3b), and the purple and blue mainly from 100 nm (Figure 3c) spheres, have to be used. An analysis of forces exerted to the spheres would be helpful to understand the underlying physics of the difference.

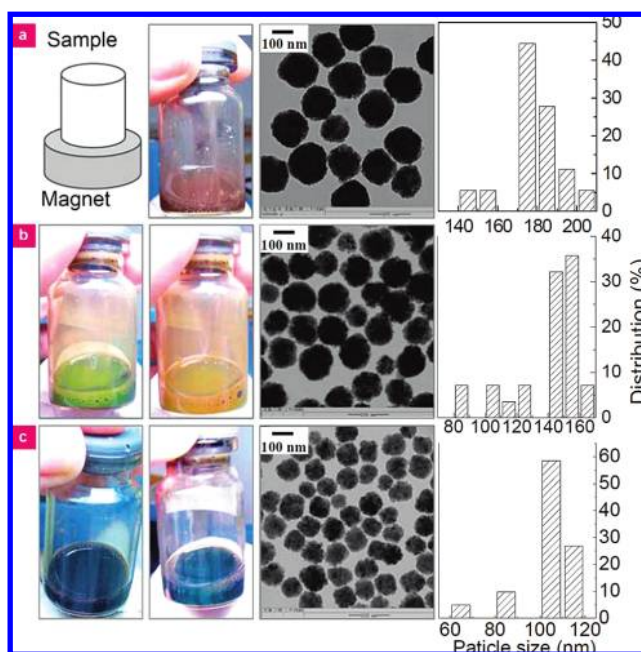


Figure 3. Characteristics of the Fe_3O_4 CPhCs of various structure colors: (a) brown, (b) green and yellow, and (c) purple and blue, all with a water-soluble photoresist as the solvent. The left column: photographs of the CPhCs in response to a varying magnetic field; the middle column: TEM (transmission electron microscopy) images; and the right column: the size distributions of consistent spheres.

TABLE 1: Parameters for Determining Forces Exerted to a Magnetic Sphere

parameters	a/nm	ϵ_1	ϵ_2	λ/nm	ζ/mV	κ^{-1}/nm	h/nm	η	ν
aqueous	77.5	80	2.58	530	-43.2	17.72	44	1	9.96×10^{-7}
polymer	77.5	2021	2.58	530	5.92	54.38	41	94	1.96×10^{-8}
μ/emu	B/G	$\nabla B/G \text{ cm}^{-1}$	F_{mp}/dyn	F_{mr}/dyn	F_{ma}/dyn	F_{f}/dyn	F_{v}/dyn	F_{er}/dyn	
1.56×10^{-13}	103	115	1.8×10^{-11}	4.66×10^{-7}	9.31×10^{-7}	1.14×10^{-8}	1.71×10^{-6}		
2.07×10^{-13}	156	145	3.0×10^{-11}	8.71×10^{-7}	1.74×10^{-6}	2.69×10^{-8}	1.49×10^{-6}		

3. Results and Discussion

Three types of forces are considered responsible for the formation and structural revolution of CPhCs. (a) The first is the electrostatic force due to the particle surface charge in aqueous solution, $F_{\text{er}} = \pi \epsilon \zeta^2 \kappa a e^{-\kappa h}$, where ϵ , ζ , and κ^{-1} denote, respectively, the dielectric constant, ζ -potential, and Debye length. a is the particle radius, and h is the surface-to-surface distance. For example, using our experimentally measured values, the electrostatic forces of a 155 nm particle in aqueous solution and polymer solution are calculated to be 1.71×10^{-6} dyn ($\epsilon = 80$, $\zeta = -43.20$ mV, $\kappa^{-1} = 17.72$ nm) and 1.49×10^{-6} dyn ($\epsilon = 2021$, $\zeta = +5.92$ mV, $\kappa^{-1} = 54.38$ nm), respectively. Interestingly, the ζ -potential shows significant change when placed in the polymer, from -43.20 to $+5.92$ mV. The potential symbol change is considered as associated with the compositional change of the electric double layers. The alcoholic hydroxyls of polyvinyl alcohol (PVA) and the unbounded carboxylate groups on the particle surface form hydrogen bonds, making the particles encircled by PVA molecules. Non-hydrogen-bonded OH groups of PVA in phosphoric acid were considered to form oxonium ions, causing the electrical property of the colloidal particles in polymer solution to be contrary to that in aqueous solution. (b) The second is the friction related to particles' movement arising from the viscosity of the resins $F_{\text{f}} = 6\pi\eta a\nu$, where η and ν denote the viscosity and the velocity of particle movement relative to the polymer, respectively. (c) The third type is the magnetic force because of the induced magnetic moment, μ . It includes (i) the dipole-dipole repulsive force, (ii) the attractive force, represented, respectively, by $F_{\text{mr}} = 3(\mu^2/d^4)$ and $F_{\text{ma}} = 6(\mu^2/d^4)$, corresponding to the planes perpendicular and parallel to the field, and (iii) a packing force that attracts superparamagnetic particles to the local maximum of the field gradient, $F_{\text{mp}} = \Delta(\mu B)$, where B is the magnetic induction.¹⁵ A typical numerical example of the magnitude of the above forces, including related parameters, is summarized in Table 1, for which several points should be clarified: (a) For calculation of F_{f} , we assumed an average position shift of the spheres for half of the lattice constant in an experimentally observed time duration of 0.1 s for aqueous solution and 5 s for polymer solution. Actually, in most cases, a static friction not only works but also plays a major role, the coefficient of which is larger than that of kinetic friction. (b) For the lattice constant, we use a 3D relaxed "close"-packing geometry, which gives interplane distance without the assumption of lattice type,¹⁶ and the PBG wavelength at green $\lambda = 530$ nm was adopted for both water and polymer solution.

Use of the polymer matrix alters the balance of forces that had been built in an aqueous solution because the forces at work, including electrostatic repulsion, static friction, and magnetic forces, are all affected. Apparently, the stability of the polymer CPhCs against vibrations was much improved due to the augmented role of static friction. Further improvement was achieved by curing the liquid polymer. Experimentally, polymer CPhCs of desired color were in situ exposed to ultraviolet light under a 120 W mercury lamp for 10 min and kept in a desiccator

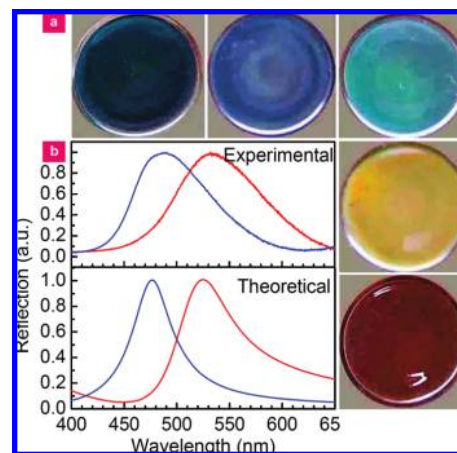


Figure 4. "Frozen" CPhC containing Fe_3O_4 spheres. (a) Photographs of samples with different colors. (b) Typical spectra of the reflection (the upper for experimental and the lower for theoretical fitting), showing the photonic band gap properties of the samples.

for several days. After polymerization, the color in the "blue" sample basically remains, whereas a slight change was found in "red" CPhCs (Figure 4a). This should be the result of cross-linking-induced volume shrinkage, which, on one hand, raises the refractive index and, therefore, blue shifts the CPhC wavelength¹⁷ and, on the other hand, distorts the lattice, broadening the spectral width in the reflection (Figure 4b): the larger the lattice constant is, the stronger distortion a sample experiences. Experimentally, an average shift of 8 nm and a broadening of 18 nm were observed, agreeing well with the theoretical prediction. Although not yet tried, elasticity as well as other mechanical and optical properties of the CPhC matrix polymer could be chosen, depending on particular needs.

4. Conclusion

We have obtained band-gap-controllable photonic crystals consisting of magnetic nanocrystal clusters in a solidified polymer matrix. The robust solid CPhC samples, possibly produced in combination with colloidal printing technology, sliced and shaped, may find wider industrial applications.

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