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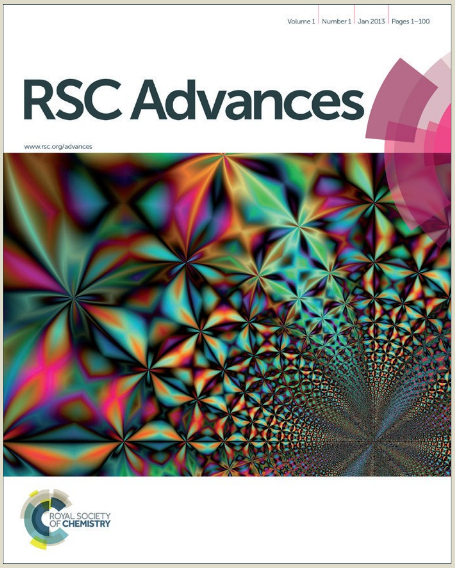

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Facile Fabrication of Magnetically Assembled Colloidal Photonic Crystal Film via Radical Polymerization

Aimei You, Yuhua Cao*, Guangqun Cao

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, 214122, P. R. China

Abstract

A facile, economical and practical technique to fabricate magnetically assembled colloidal photonic crystal in the polyacrylamide hydrogel matrix was demonstrated by an instant radical polymerization. By taking advantage of the instantaneousness of magnetic assembly, the magnetic colloids were successfully assembled into photonic crystal structures with tunable stop bands in aqueous solution. The Bragg diffraction color could be simply controlled by tuning the strength of the external magnetic field to fulfill the diffraction covering the entire visible spectrums. An appropriate amount of ionic initiator APS was a key in radical polymerization of photonic crystal hydrogel film. 0.3 mg/mL of APS was chosen, not only to meet a rapid formation of the polyacrylamide hydrogel, but also not to lead to coagulation of these magnetic colloids in the hydrogel. Due to the significantly instant property of magnetic assembly and radical polymerization, coagulation of these magnetic assemblies owing to the long time exposure to an external magnetic field could be prevented. Therefore, the photonic crystal hydrogel film with uniform diffraction color could be obtained. Notably, the flexible hydrogel film displayed obvious deformation responsiveness.

The diffraction light got red-shifted as the level of the deformation rose. The achievement in immobilization endows the system a major stride toward practical applications in responsive photonic materials.

Keywords: magnetic colloids; magnetic assembly; photonic crystal structure; radical polymerization

Introduction

Photonic crystals, especially self-assembled from monodispersed colloids with magnetic constitute, have been the focus of intensive research due to the promising and potential applications in light controlling and manipulating fields.[1-3] Responsive photonic crystals whose diffraction wavelength and intensity can be tuned by the external stimuli present intriguing applications in photonic fields including bio- and chemical sensors[4-6], color displays[7, 8] and anti-counterfeiting labels[9-12]. Responsive photonic crystal has been applied in the environmental fields, since the environmental problem is increasingly serious. Wang et al.[13] described various of responsive photonic crystals designed to detect the environmental pollutants. Liu et al.[14] developed a series of patterning responsive one-dimensional photonic crystals for sensing acidic/alkali vapors by the naked eye. A variety of self-assembly processes driven by gravitation, centrifugal force, hydrodynamic flow, electrophoretic deposition, capillary force, and electrostatic interaction have been reported to construct colloidal photonic crystal structure.[15, 16] Unlike those time consuming methods aforementioned, magnetic assembly strategy has been found to be an effective route for rapid control of the assembly behaviors. The instantaneous and contactless characteristics of magnetic interaction permit speedy and independent experimental process.[17]

Bibette et al.[18] pioneered the application of magnetic field to assemble the uniform emulsion droplets containing ferrofluids into 1D chains with tunable optical diffractions. Later, Asher et al.[19, 20] reported their achievements in the fabrication of superparamagnetic photonic crystal with tunable optical properties with the assistance of external magnetic field. Generally, there are two types of magnetic forces on magnetic colloidal particles with an external magnetic field, the dipole-dipole force and the packing force.[21] The dipole-dipole interaction can be attractive or repulsive, depending on the angle between the direction of the external magnetic field and the line connecting the center of the two particles. When the dipole interaction energy is large enough to overcome thermal fluctuations, 1D chain-like structures can be induced. The packing force could be understood as the interaction of a magnetic dipole with the external magnetic field. When the magnetic field is applied for enough long time, the packing force can induce the 1D chains to transform into 3D structures. Whereas, with the increase of the exposure time in a magnetic field further, a disorder of the magnetically assembled structures could occur.

The magnetic nanoparticles as the building blocks to assemble photonic crystal is an effective and convenient means with an external magnetic field. However, the magnetic field can offer stimuli only as the photonic crystal is in a liquid or mobile form. The photonic crystal in liquid solution state is inconvenient in practical application, and hampers the further progress. Yin et al.[16, 22-24] had successfully embedded $Fe_3O_4@SiO_2$ colloids into polymer matrix. However, these photonic crystal did not work in an aqueous solution owing to the high polarity of water. Therefore, it is still a challenge to immobilize the magnetically assembled colloidal photonic crystals in aqueous solution.

In the present work, we reported a facile, economical and practical strategy to lock the magnetically assembled colloidal photonic crystal structure into a polyacrylamide hydrogel matrix. Combined the instant property of magnetic assembly with radical polymerization, a hydrogel film with uniform diffraction color could be obtained. Furthermore, a UV photopolymerization strategy was also used to prepare the hydrogel film, and a comparison between the two polymerization methods was conducted.

Experimental Section

Materials. $FeSO_4 \cdot 7H_2O$, $FeCl_3$ $6H_2O$, oleic acid (OA), sodium dodecyl sulfate (SDS), methyl methacrylate (MMA), potassium peroxydisulfate (KPS), ammonium persulfate (APS), acrylamide (AM), and all other inorganic salt and organic solvents were of analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd.

(China). N,N'-methylenebis(acrylamide) (BIS), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), ethyleneglycol dimethacrylate (EGDMA >98%), and N,N,N',N'- tetramethylethylenediamine (TEMED) were purchased from Rotrn Shanghai Biological Technology Co., Ltd. (China). All solutions were prepared with ultra-pure water (18.2 MΩ cm) from a NW Ultra-pure Water System (Heal Force, Nison Instrument, China).

Preparation of polyacrylamide hydrogel film embedded photonic crystal structures. Fe_3O_4@OA magnetic nanoparticles were synthesized by the modified classical chemical co-precipitation procedure.[25] Magnetic composite nanoparticles (MCNPs) were then prepared following a three-step miniemulsion polymerization.[26] The particles were collected by magnetic separation, washed with ultra-pure water for several times, and finally dried under vacuum at 60℃ for 2h to get the MCNPs. The pre-polymerization solution was composed of AM monomer (0.8 g), BIS cross-linker (0.005 g), APS initiator (0.0015 g) and ultra-pure water (5 mL). The mixture solution was stirred with a magnetic stirrer until the reactants were dissolved completely. Then, MCNPs (0.025 g) were added into the mixture, and sonicated for 2 min until the solution was homogeneous. After that, TEMED accelerator (50 µL) was added into the solution and stirred rapidly for 10 s. Finally, under a magnetic field, the mixture solution remained at undisturbed state for 10 s to complete polymerization as well as magnetic assembly of photonic crystal structure. A hydrogel film containing magnetically assembled colloidal photonic crystal structure was constructed.

The procedure using UV photopolymerization was the same as using radical polymerization except replacing the initiator APS with photoinitiator Irgacure 2959 (0.02 g) and omitting the accelerator TEMED. The mixture solution was placed in a magnetic field and exposed to UV radiation for 1 h to implement assembly and polymerization simultaneously.

Characterization. The photographs were taken with a digital camera (Canon, EOS Kiss X4). The average diameter and surface potential of the final composite nanoparticles latex were measured by Zeta potential and nanometer particle analyzer (ZetaPALS; Brookhaven Instruments Corporation, USA). The morphology of the particles were characterized by the transmission electron microscopy (TEM, JEOL, Japan) at a 200 KV accelerating voltage. The Bragg diffraction spectrums were recorded by a miniature fiber optic spectrometer (FLA 5000+, China).

Results and discussion

MCNPs with various hydrodynamic sizes were synthesized by altering the amount of SDS used in the three-step miniemulsion polymerization process (see Supplementary Table S1). In a typical experiment, MCNPs with a hydrodynamic size of ca.151 nm were used to construct the photonic crystal structures. Without cleaning, the MCNPs aqueous solution could not show Bragg diffraction color even under a very strong magnetic field. The phenomenon could be ascribed to the high ionic strength of the magnetic colloids solution. After cleaning, MCNPs could be dispersed in water and showed a reversible tunable optical response with an external magnetic field. The optical Bragg diffractions resulted from the formation of periodically ordered structures of MCNPs colloids along the magnetic field. Fig. 1 was a representative TEM image of MCNPs, which sample was prepared under a magnetic field. Obviously, MCNPs could be assembled into periodic arrangement photonic crystal structure upon a magnetic field. It also showed that the MCNPs had a distinct core-shell structure, where magnetite nanoparticles as the core material and polymethyl acrylate polymer constituted for the shell structure. MCNP structure was illustrated in Schematic 1. Firstly, oleic acid bound to the surface of Fe_3O_4 particles through the strong coordination of carboxylate groups with iron cations. The long alkyl chain of OA on the surface of magnetite gave the particles hydrophobicity. Then, Fe_3O_4@OA magnetic nanoparticles coexisted with hydrophobic monomer and cross-linking agent inside miniemulsion droplets by sonification process. The miniemulsion droplets could be regarded as a microreactor, the polymerization reaction proceeded within the droplets once the initiator was added. Finally, MCNPs were obtained, where the magnetic core embraced by the polymer shell. The sulfate ions dissociated from SDS and KPS adsorbed on the surface of MCNPs and rendered the particle surfaces highly negative charged. The average surface potential of MCNPs was -57.5 mV (RSD 0.29%, n=10). The peak at 1260 cm^{-1} would be characteristic peak of S=O stretching vibrating in FT-IR spectrum shown in Supplementary Fig. S1, which had a good agreement with the previous analysis.

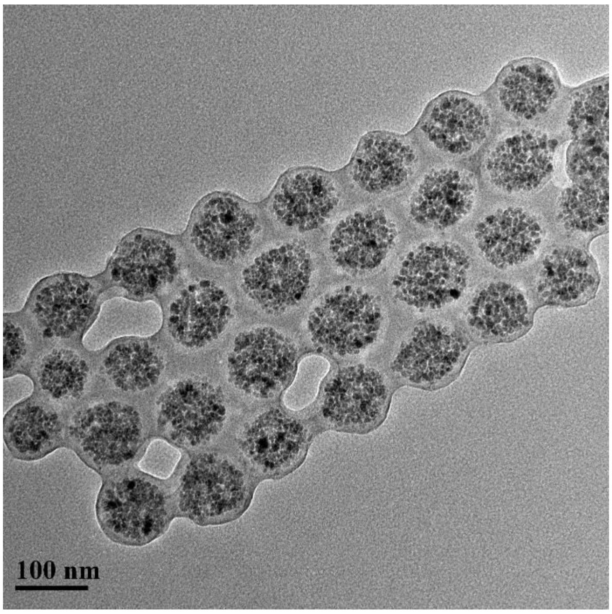
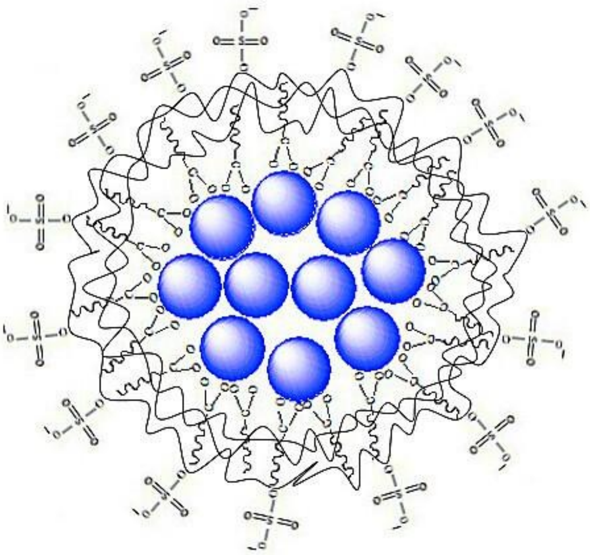


Fig. 1 TEM of MCNPs assembled into photonic crystal structures



Schematic 1 The illustration of MCNP structure.

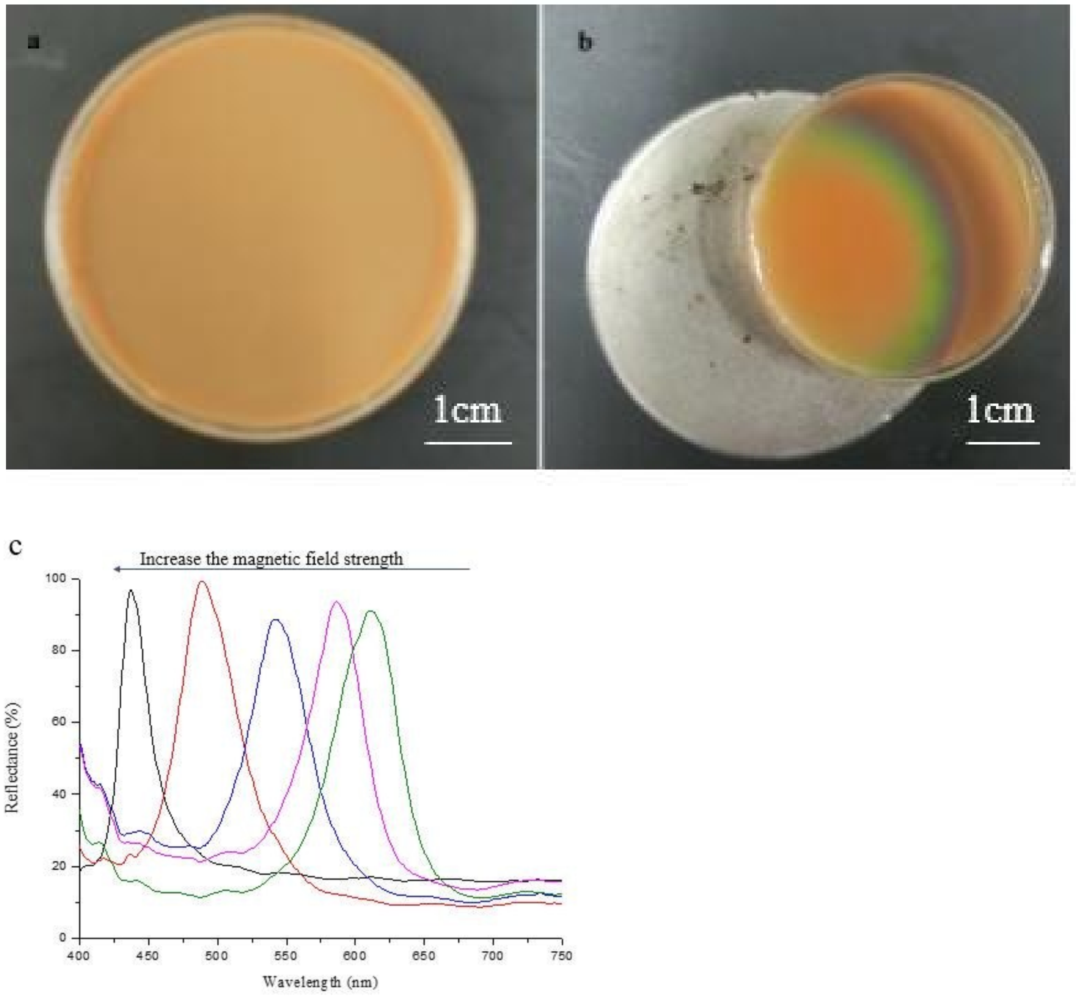
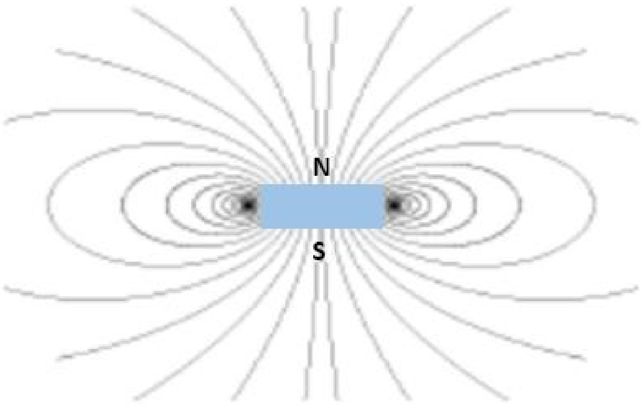


Fig. 2 Photographs and reflection spectra of MCNPs solution.

(a) Photograph of MCNPs solution in absence of magnetic field and (b) upon an external magnetic field. (c) Reflection spectra at normal incidence of the MCNPs solution in response to different strength of magnetic fields.



Schematic 3 Spatial distribution of the applied magnetic field

Fig. 2 showed the optical photographs and reflection spectra of an aqueous solution of MCNPs in response to a magnetic field. Without magnetic field, the MCNPs solution was brown, shown in Fig. 2a. With a disc NdFeB magnet, the MCNPs solution displayed an iridescence color, shown in Fig. 2b. The spatial distribution of the applied magnetic field was showed in schematic 3, which was the longitudinal cross section figure of the disc magnet. The magnetic field strength in the same plane is not uniform, it has an increasing trend from the center to the edge. Correspondingly, diffraction wavelength became shorter, and the color changed from orange to purple. In the rightmost section, the color restored to its original brown without the magnetic field. Fig. 2c showed a blue-shift from 611 nm to 438 nm as increasing the magnetic field strength by adjusting the distance between the magnet and the solution from 4.0 cm to 0 cm. The application of a magnetic field influenced the magnetic colloids in the solution in two types of magnetic forces, the dipole-dipole force and the packing force. When the magnetic force and the strong repulsive electrostatic force due to the high density negative charges reached at a balanced state, the photonic crystal structure could be constructed. The distance between the particles determined the color of the diffraction light resulted from the ordered structures. By adjusting the equilibrium of attractive and repulsive forces, the interparticle distance could be controlled, resulting in the magnetically tunable stop bands covering the entire visible spectrums.

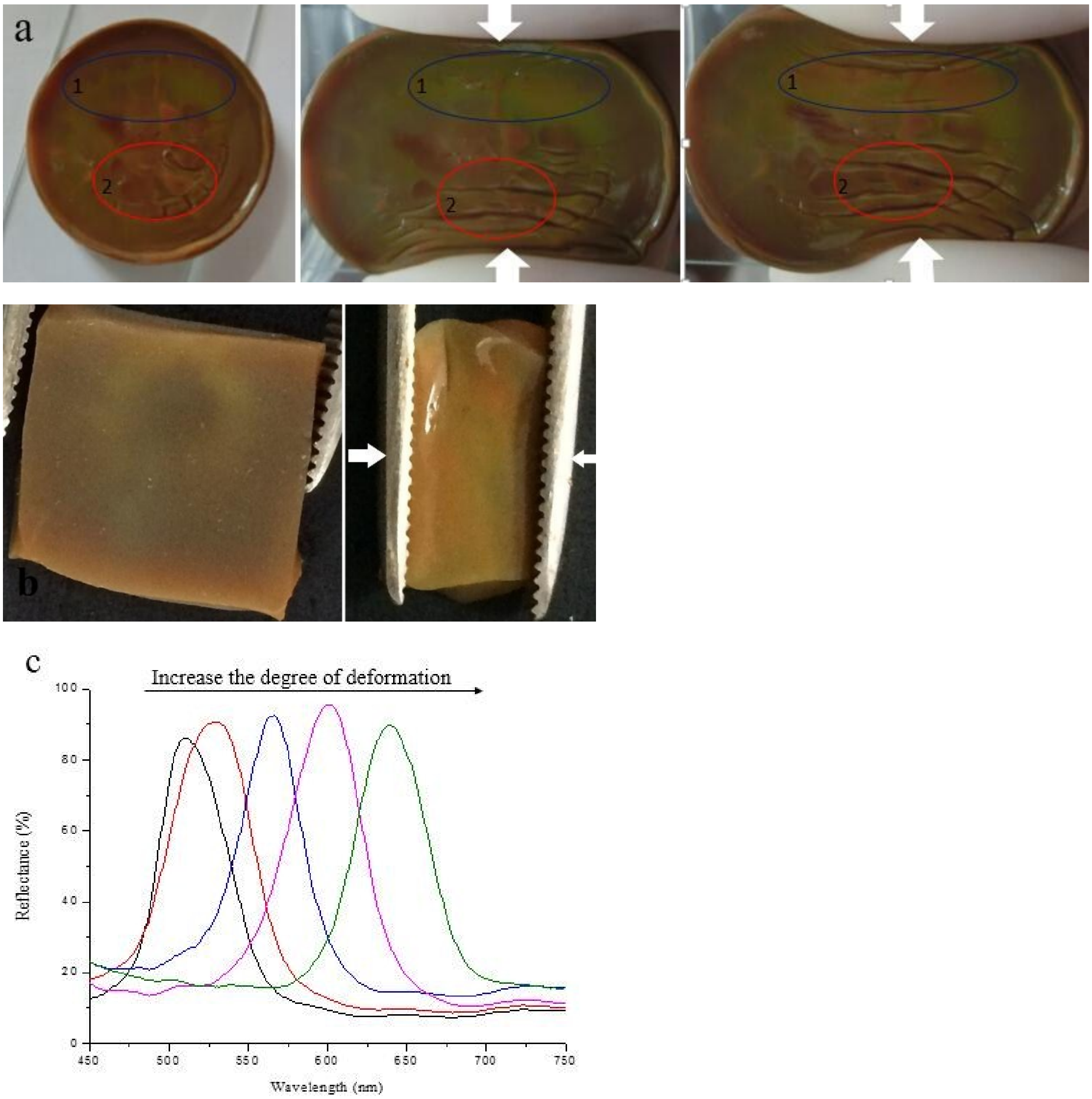
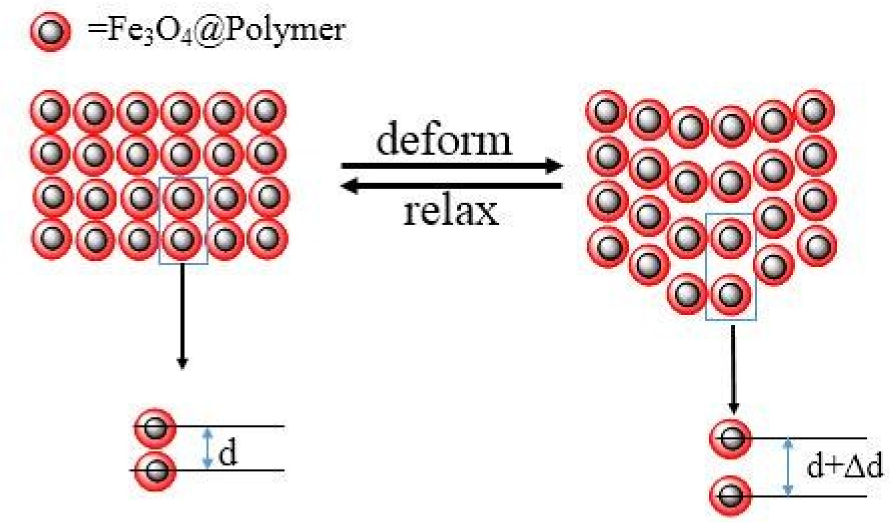


Fig. 3 Photographs and reflection spectra of the flexible polyacrylamide hydrogel films. (a) Photograph of the hydrogel film synthesized with UV photopolymerization. (b) Photograph of the hydrogel film synthesized with radical polymerization. (c) Corresponding reflection spectra of the hydrogel film at normal incidence upon the different degrees of deformation.

Though these liquid-phase magnetically assembled colloids photonic crystal could be obtained easily, it would be transiently disordered when the magnetic field was withdrew. Furthermore, because these photonic crystals were formed and stabled based on electrostatic repulsion, the photonic crystal structures could also be disordered once changing the environmental conditions, such as pH, ionic strength and solvent. Inorganic salts introduced to adjust the pH or ionic strength would screen the interparticle repulsive interactions, while solvents have the solvation effect that could influence the balance equilibrium. It is an intrinsic limitation of the electrostatic-stabilized magnetically assembled colloidal photonic crystal. As a consequence, immobilization of magnetic colloids photonic crystal structure in a liquid state has been a challenge in the research area. We have solved the problem by embedding photonic crystal structure in a polyacrylamide hydrogel network. Although all of the monomer acrylamide, the cross-linker BIS and the accelerator TEMED are nonionic substances, the indispensable initiator APS is ionic. An appropriate amount of ionic initiator APS was a key in radical polymerization of the hydrogel film containing magnetic photonic crystals. Because the electrostatic-stabilized photonic crystal system could not tolerate a large ionic strength, so ionic APS should be limited in the electrostatic-stabilized photonic crystal system. The effect of APS concentration ranged from 0.1 mg/mL to 0.5 mg/mL on the polymerization of the hydrogel and the stability of the system were investigated. As APS concentration of 0.05 mg/mL, the hydrogel could not formed. AS APS concentration between 0.1 mg/mL and 0.2 mg/mL, the reaction time was 2-4 min. When APS concentration of 0.3 mg/mL, the time needed to form hydrogel was nearly 1 min. Increasing APS concentration further, the reaction time did not reduce obviously. However, as APS concentration reached 0.5 mg/mL, the magnetic nanoparticles started to coagulate. The high concentration of APS would screen the charge of the magnetic nanoparticles, and lowered down the stability. Therefore, comprehensively considering the reaction time and ionic strength, 0.3 mg/mL was chosen as the optimal APS concentration. A short reaction time could avoid the magnetic particles exposed in the magnetic field for a long time. A relative low concentration of ionic APS would ensure the stability of the magnetically assembled colloidal photonic crystal system.

A perfect flexible polyacrylamide hydrogel film could be achieved as the molar ratio of monomer AM to cross-linker BIS was appropriate. As shown in Fig. 3a, the hydrogel film was synthesized with UV photopolymerization. It displayed light green color at a relaxed state in partial zone, because the magnetic assembly process and polymerization process had completed simultaneously. The color responsive process could be seen clearly from the selected circle section (1) marked in blue in Fig.3a. Once upon squeezing force, the diffraction color became red shifted, from light green to yellow-green and then orange-red with increasing the degree of deformation. Albeit the structure color has been fixed in the hydrogel matrix, the color area was local. The selected circle section (2) marked in red in Fig.3a displayed its original brown color and did not show any obvious change in the process of deformation. The result implied where photonic crystal structure was failed to be constructed. The phenomenon of nonuniform structure color was owing to the inhomogeneous intensity of the magnetic field and a long time exposure in the magnetic field. Owing to exposure in the magnetic field for enough long time, the magnetic packing force could drive the MCNPs to move towards regions with maximum magnetic field strength, inducing the crystallization or even coagulation. These defects hindered the practical application of UV polymerization strategy. Hence, the radical polymerization strategy was considered for the instant nature of the reaction. Fig. 3b was the hydrogel film obtained from radical polymerization. At a relaxed state, uniform weak purple color could be seen, owing to the formation of photonic crystal structure in the hydrogel matrix. While at a squeezed state, distinct red-shift from weak purple to orange-red could be distinguished with the naked eye. The peak of diffraction wavelength red-shifted from 510 nm to 630 nm. Therefore deformation was the factor to trigger the change of diffraction color. The red-shift of diffraction wavelength could be explained as a consequence of the changing of the lattice constant d upon squeezing the polymer matrix, as suggested by the model in Schematic 2. The model illustrated the deformation responsive principle. As the hydrogel film deformed, the structure of the unit cell of the photonic crystal changed correspondingly. From the reflection spectra, the corresponding values for the interparticle distance in response to deformation increased from 191 nm to 236 nm, estimated by Bragg's Law $\lambda=2nd\sin\theta$, where 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 [19, 27]. The fabrication of the photonic hydrogel film via radical polymerization was simpler and quicker than with the photopolymerization.



Schematic 2 Mechanism of deformation and the structure of the unit cell

Conclusion

Colloidal photonic crystal structures with tunable stop bands covering the entire visible spectrums have been constructed in aqueous solution by taking advantage of the instant nature of magnetic assembly. The equilibrium of electrostatic repulsive force and magnetic attractive force contributed to the orderly periodic structure. The Bragg diffraction colors could be controlled simply by tuning the strength of the external magnetic field. The optical response to the external magnetic field was fast and fully reversible. An appropriate amount of ionic initiator APS was a key in radical polymerization of photonic crystal hydrogel film. The lowest APS concentration required for formation of the polyacrylamide hydrogel and the highest APS concentration where the photonic crystal system could be stable have been investigated. Comprehensively considering the effect of reaction time and ionic strength, 0.3 mg/mL was chosen as the optimal APS concentration. A polyacrylamide hydrogel matrix with diffraction colors has been achieved to lock the magnetically assembled colloidal photonic crystal structure. Notably, the flexible hydrogel embedding magnetically assembled colloidal photonic crystal has a rapid and reversible color responsiveness to deformation. The achievement in immobilization of colloidal photonic crystal structures in liquid state endows the system a major stride toward practical applications in responsive photonic materials.

Author Information

Corresponding Author.

Tel.: +86 510 85917090

Email address: yuhuacao64@gmail.com (Yuhua Cao)

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Notes and references

1. J. Ge and Y. Yin, *Angewandte Chemie*, 2011, **50**, 1492-1522.
2. K. Matsubara, M. Watanabe and Y. Takeoka, *Angewandte Chemie*, 2007, **46**, 1688-1692.
3. M. K. Maurer, I. K. Lednev and S. A. Asher, *Adv Funct Mater*, 2005, **15**, 1401-1406.
4. L. Bai, Z. Xie, W. Wang, C. Yuan, Y. Zhao, Z. Mu, Q. Zhong and Z. Gu, *ACS nano*, 2014, **8**, 11094-11100.
5. K. I. MacConaghy, C. I. Geary, J. L. Kaar and M. P. Stoykovich, *Journal of the American Chemical Society*, 2014, **136**, 6896-6899.

6. B. Ye, H. Ding, Y. Cheng, H. Gu, Y. Zhao, Z. Xie and Z. Gu, *Advanced materials*, 2014, **26**, 3270-3274.
7. Z. Liu, Q. Zhang, H. Wang and Y. Li, *Chemical communications*, 2011, **47**, 12801-12803.
8. H. Ding, Y. Cheng, H. Gu, Y. Zhao, B. Wang and Z. Gu, *Nanoscale*, 2013, **5**, 11572-11576.
9. H. Hu, J. Tang, H. Zhong, Z. Xi, C. Chen and Q. Chen, *Scientific reports*, 2013, **3**, 1484.
10. H. S. Lee, T. S. Shim, H. Hwang, S.-M. Yang and S.-H. Kim, *Chemistry of Materials*, 2013, **25**, 2684-2690.
11. R. Xuan and J. Ge, *J. Mater. Chem.*, 2012, **22**, 367-372.
12. J. Y. Shieh, J. Y. Kuo, H. P. Weng and H. H. Yu, *Langmuir : the ACS journal of surfaces and colloids*, 2013, **29**, 667-672.
13. F. Wang, Z. Meng, F. Xue, M. Xue, W. Lu, W. Chen, Q. Wang and Y. Wang, *Trends in Environmental Analytical Chemistry*, 2014, **3-4**, 1-6.
14. C. Liu, C. Yao, Y. Zhu, J. Ren, K. Lan, H. Peng and L. Ge, *RSC Advances*, 2014, **4**, 27281.
15. L. He, Y. Hu, H. Kim, J. Ge, S. Kwon and Y. Yin, *Nano letters*, 2010, **10**, 4708-4714.
16. H. Kim, J. Ge, J. Kim, S.-e. Choi, H. Lee, H. Lee, W. Park, Y. Yin and S. Kwon, *Nature Photonics*, 2009, **3**, 534-540.
17. M. Wang, L. He and Y. Yin, *Materials Today*, 2013, **16**, 110-116.
18. J. Bibette, *J Magn Magn Mater*, 1993, **122**, 37-41.
19. X. L. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich and S. A. Asher, *Chemistry of Materials*, 2002, **14**, 1249-1256.
20. X. L. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich and S. A. Asher, *Advanced materials*, 2001, **13**, 1681-1684.
21. J. Ge, L. He, Y. Hu and Y. Yin, *Nanoscale*, 2011, **3**, 177-183.
22. J. Ge and Y. Yin, *Advanced materials*, 2008, **20**, 3485-3491.
23. J. P. Ge, H. Lee, L. He, J. Kim, Z. D. Lu, H. Kim, J. Goebl, S. Kwon and Y. D. Yin, *Journal of the American Chemical Society*, 2009, **131**, 15687-15694.
24. Y. Hu, L. He, X. Han, M. Wang and Y. Yin, *Nano Research*, 2015, **8**, 611-620.
25. L. F. Shen, P. E. Laibinis and T. A. Hatton, *Langmuir : the ACS journal of surfaces and colloids*, 1999, **15**, 447-453.
26. L. Zhu, X. Yang and Y. Cao, *Analytical Letters*, 2013, **46**, 982-998.
27. J. Ge, Y. Hu and Y. Yin, *Angewandte Chemie*, 2007, **46**, 7428-7431.