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Magnetic Nanomaterials

# Magnetically Responsive Photonic Nanochains**

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Responsive photonic materials are of great interest owing to their broad applications that are relevant to the controlling of colors.[1] Being efficient and inexpensive, colloidal self-assembly has been widely studied for the fabrication of photonic crystal structures, especially for applications that can tolerate defects.[2] While many studies have focused on tuning the refractive index of the components or the periodicity by incorporating active materials that can respond to environmental changes,[3] we have recently developed a magnetically tunable photonic structure by assembling uniform superparamagnetic (SPM) colloidal particles into one-dimensional (1D) chain-like arrays in various liquid media.[4] The dynamic ordering of the magnetic colloids with controllable periodicity along the direction of the external field renders the system a fast, fully reversible photonic response across the visible–near-infrared spectrum. By taking advantage of the magnetic property, we have also developed tunable photonic materials with properties that can be manipulated by changing their orientation with external fields.[5] This was achieved by embedding aligned chains of periodically arranged SPM particles in polymer microspheres so that their relative orientation and correspondingly the diffraction property can be tuned by rotating the external magnetic fields. The division of bulk photonic crystals into many small units of tens of micrometers in size brings the benefits of easy fabrication, actuation, and broader applications, as the color of these units can be controlled individually or collectively as needed by using external magnetic fields. It has been our great interest to extend this principle to the fabrication of magnetically responsive photonic structures with significantly reduced dimensions so that color manipulation with higher resolution can be realized. The ideal case is to fix individual magnetic particle chains, which will produce the smallest possible photonic nanostructures that can effectively diffract at visible spectrum. In addition to color displays, these optically active magnetic nanochains may find great use in fields such as biological and chemical sensing and biomedical labeling and imaging.[6]

Herein, we present a convenient and flexible approach for the fabrication of individually fixed nanochains with a magnetically responsive photonic property by combining magnetic assembly with sol–gel processes. The superparamagnetic $Fe_3O_4$ colloidal nanocrystal clusters (CNCs) are initially coated with a thin layer of silica, then assembled into chains by applying a magnetic field, and the chains are then further overcoated with an additional layer of silica to stabilize the chain structure. The key is to induce the chaining of the magnetic particles by brief exposure to external fields during the silica coating process so that the particles stay temporarily connected, allowing additional silica deposition to fix the chains into mechanically robust rods or wires. The process is highly controllable: the periodicity can be varied by using $Fe_3O_4$ CNCs of different sizes, the interparticle spacing can be fine-tuned by adjusting the timing of magnetic field exposure, and the length of the chains can be controlled by changing the duration of the magnetic field exposure. The resulting photonic chains disperse randomly in solution in the absence of a magnetic field, but align themselves and show diffraction color instantly when an external field is applied. The fixed photonic nanochains exhibit long-term structural/optical stability and can be conveniently incorporated into many liquid or solid matrices.

Figure 1 illustrates the fabrication process for the $Fe_3O_4@SiO_2$ photonic chains. $Fe_3O_4$ CNCs are synthesized using a high-temperature hydrolysis reaction that we reported previously.[4c] After cleaning, the aqueous dispersion of $Fe_3O_4$ particles is mixed sequentially with ammonium hydroxide ($NH_4OH$) and ethanol. As the $Fe_3O_4$ CNCs are covered with a layer of polyacrylate (PAA), they tend to aggregate in ethanol; this aggregation can be temporarily broken up under sonication. Tetraethoxysilane (TEOS) is injected after the dispersion is quickly transferred into a flask under mechanical stirring. Upon hydrolyzation and condensation, a thin layer of silica starts to deposit on the surface of the $Fe_3O_4$ particles, thus gradually improving their dispersity in

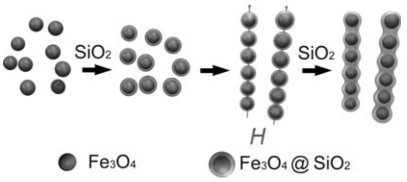

**Figure 1.** Illustration of the fabrication process of the fixed 1D nanochains containing periodically arranged $Fe_3O_4$ particles. The key is to induce chaining of the uniform magnetic particles by a brief magnetic field exposure *H* during the silica coating process and then to allow additional silica deposition to further stabilize the chain structures. The timing and duration of magnetic exposure can be used to conveniently control the length and periodicity of the nanochains.

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ethanol.[7] If the silica layer is allowed to continuously grow beyond 20 nm in thickness, the resulting $Fe_3O_4@SiO_2$ core–shell particles become highly dispersible in ethanol solutions. However, if a magnetic field is applied during the initial stage of silica coating, the magnetic dipole–dipole interaction brings the particles together to form 1D chains. Owing to their low dispersibility, the particles tend to remain in the linear chain structure even after the external field is removed. We believe the connection between neighboring particles may also be enhanced through the condensation reaction of surface silanol groups on the growing silica surface.[8] Continued deposition of silica covers the entire surface of each chain, producing peapod-like structures with further increased mechanical stability.[9] The final products are 1D chains containing periodically arranged uniform $Fe_3O_4$ CNCs that can effectively diffract visible light.

The strength of magnetic field is an important parameter for the successful fabrication of photonic nanochains. The magnetic field should be strong enough to induce chaining of magnetic particles and overcome the electrostatic force to ensure close contact of neighboring particles before additional silica coating. As reported previously, the required field strength decreases with increasing size of magnetic CNCs.[4b] For medium-sized (ca. 160 nm) particles, a field strength of 570 G is used. If the field strength is too high (> 900 G), the magnetic particles will aggregate immediately into large objects without retaining the chain structure. Furthermore, a uniform magnetic field is required for producing photonic chains with uniform lengths. This has been achieved by simply using the central portion of a large-diameter disk magnet, although further improved field uniformity might be possible with specially designed electromagnets.

The chain structure was characterized by using both scanning (SEM) and transmission electron microscopy (TEM). As shown in Figure 2 a, b, the product deposited on a silicon substrate clearly shows 1D chain structures, which appear in the form of many linearly connected spheres. The core–shell structure can be better observed in the TEM image in Figure 2 c. The periodically arranged $Fe_3O_4$ cores and the smooth silica coating can be identified by the contrast between the core and the shell. Note that the magnetic cores are not in direct contact with each other, confirming the initial silica deposition before the chain formation.

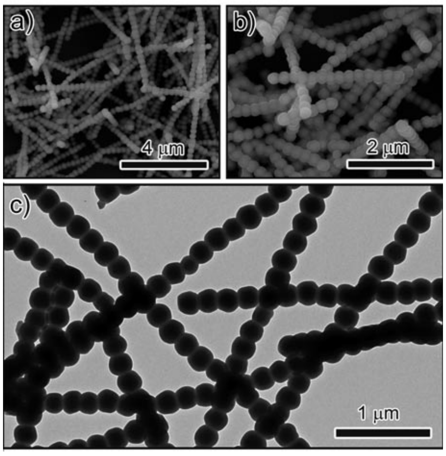

*Figure 2.* a, b) SEM and c) TEM images of typical photonic nanochains. The particle chains are permanently fixed by silica coating so that they remain stable when dispersed in solution or dried on solid substrates.

The photonic chains can diffract visible light and display brilliant colors owing to the periodic arrangement of the $Fe_3O_4$ particles. In the absence of external magnetic fields, the chains are randomly oriented so that their bulk solution only shows the native brown color of iron oxide. When an external field is applied, all the chains are aligned along the field direction so that the dispersion shows distinctive colors. We used an optical microscope operated in dark-field mode to clearly observe the magnetic alignment of the chains and the corresponding photonic response. Without the influence of a magnetic field (Figure 3), the chains are randomly dispersed in solution so that no uniform colors can be observed. When a vertical magnetic field is applied, all of the chains align along the field direction and appear as brightly colored dots to the viewer. All the photonic chains within one sample show a single color because the particles arrange in the same periodicity.

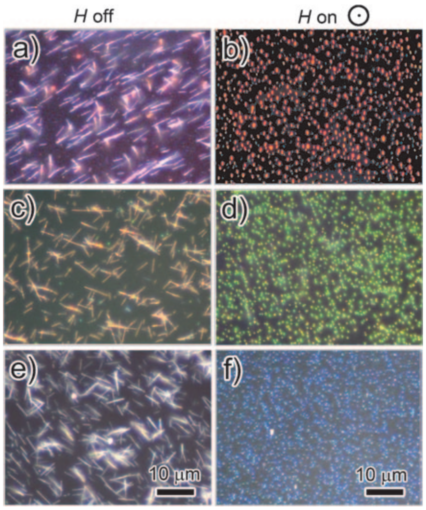

*Figure 3.* Dark-field optical microscopy images of magnetic photonic chains with different diffraction colors switched between "off" (a, c, e: without magnetic field) and "on" (b, d, f: with vertical magnetic field) states. These photonic chains diffract at different wavelengths because they were prepared using $Fe_3O_4$ CNCs of different average sizes: a, b) 182 nm, c, d) 160 nm, e, f) 113 nm. All images are at the same scale.

In a similar fashion to the magnetic particle arrays that we reported previously, the diffraction wavelength of the photonic chains can be controlled through the periodicity of the particle arrays. A convenient way to change the periodicity is to use $Fe_3O_4$ CNCs of different sizes. As shown in Figure 3, photonic chains assembled from large CNCs (ca. 182 nm in diameter) diffract red light, while those from medium-sized particles (ca. 160 nm) diffract green light and those from small CNCs (ca. 113 nm) tend to diffract blue light. As we reported previously, uniform CNCs can be produced with average diameters ranging from about 30 to 200 nm,[4c] so it should be

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possible to produce photonic chains with diffraction wavelengths across a wide range of spectrum from near UV to near IR.

The timing of magnetic field exposure is critically important to the success of the chain fixing. The magnetic field needs to be applied when the surface of the $F_3O_4$ has been covered with a thin silica layer, which is typically about 5 min after the addition of TEOS. Exposing the dispersion to magnetic field too early will result in large irregular aggregates because of the low dispersity of the particles in solution. On the other hand, exposure to magnetic field must be carried out before the particles gain high dispersity in solution, which typically occurs when the thickness of the silica layer is above 20 nm. Otherwise, the particle chains temporarily formed by brief magnetic exposure cannot be maintained during the subsequent additional silica coating. Interestingly, controlling the timing of magnetic exposure also allows for the fine-tuning of the interparticle spacing within photonic chains. Because silica deposition is a slow and continuous process, the thickness of the initial silica layer varies when the magnetic field is applied at different times. If the magnetic field is applied at a later stage, a relatively thicker silica layer is deposited, resulting in a larger interparticle spacing and subsequently diffraction at a longer wavelength. Figure 4a shows TEM images of photonic chains produced from CNCs with a diameter of about 160 nm by applying external magnetic fields at different times. The interparticle separation gradually increases when the timing of magnetic exposure changes from 6 to 8, 10, 11, and 16 min after injecting TEOS. Figure 4b and c summarize the interparticle separation $d$ and the diffraction wavelength $\lambda$ of these five samples. The application of a magnetic field at an early stage (6 min) results in a thin layer of silica between neighboring particles ($d = 12.8$ nm) and thereby diffraction at a relatively short wavelength (ca. 517 nm). When the magnetic field is applied at a later stage (16 min), the interparticle separation increases to about 39.1 nm and the diffraction red-shifts to about 593 nm. According to Bragg's equation, the diffraction wavelength is proportional to the periodicity $D$ according to $\lambda = 2nD$ (at normal incidence of light). This is verified by plotting $\lambda$ against $D$ (inset in Figure 4c), which reveals a perfect linear relationship. The effective refractive index $n$ of the system calculated from the slope of the linear fit of the plot is 1.43. Because the chain structure cannot be retained when the initial silica coating is beyond 20 nm in thickness, the silica layer between neighboring CNCs can only be tuned within the limit of 10–40 nm with the corresponding diffraction peak shift in the range of about 80 nm.

The chain length can be tuned over a range of two to tens of micrometers by adjusting the magnetic field duration from about 0.5 s to about 4 s, as shown in Figure 5. Upon a very brief exposure (0.5 s) to an external field, the $Fe_3O_4$ CNCs only assemble locally to form short chains two micrometers in length (Figure 5a). Increasing the field duration allows more extensive particle assembly and chain recombination, producing longer chains with lengths of several tens of micrometers (Figure 5b–d). Retaining the dispersion in the magnetic field for an even longer time leads to random aggregation of the chains.

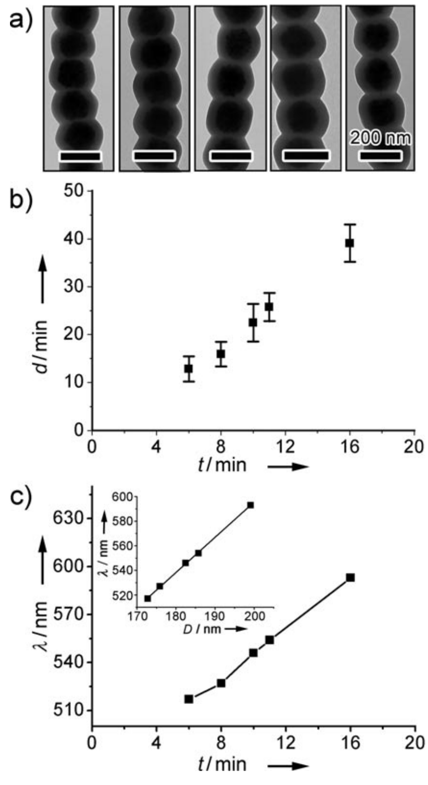

**Figure 4.** a) Representative TEM images of photonic chains with different interparticle separation controlled by applying magnetic fields at different times after injecting TEOS (left to right: 6, 8, 10, 11, 16 min). All scale bars correspond to 200 nm. b) The dependence of interparticle separation $d$ on the time-point of magnetic field exposure $t$. c) The dependence of diffraction wavelength of the photonic chains on the timing of magnetic exposure. Inset: the diffraction wavelength $\lambda$ versus the periodicity $D$ of the photonic chains.

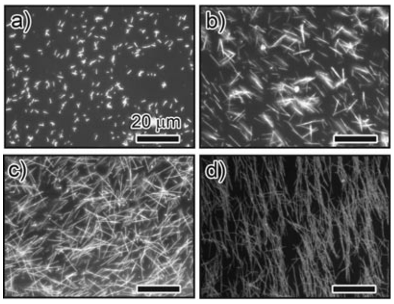

**Figure 5.** Dark-field optical microscopy images of photonic chains with different lengths obtained by applying a magnetic field for different durations: a) 0.5, b) 1, c) 2, d) 4 s. The field strength of magnetic exposure is estimated to be about 570 G and field gradient about 197 G $cm^{-1}$. All images are at the same scale.

As photonic chains contain many magnetic particles, they show high sensitivity to external magnetic fields. We have observed a measurable reflection with an intensity of 4.5% owing to partial chain alignment upon the application of a low magnetic field of only about 4 G, while in our previously reported unfixed system a minimum of 50 G is typically

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required for observable diffraction because magnetic particles first need to be assembled from the dispersed form into periodic arrays. In the current system, a magnetic field of 50 G is sufficient to align all the photonic chains along the field direction, producing diffraction with a maximum intensity. Because the switching of the diffraction only involves chain rotation, it can be accomplished rapidly (within a second) and reversibly in a sufficiently strong magnetic field (>50 G). Another good feature of the current system is the optical stability. The photonic chains remain separated from each other in magnetic fields owing to the magnetic repulsive force perpendicular to the field direction. We have observed a stable diffraction (in both intensity and wavelength) over a period over 4 h for photonic chains aligned in a magnetic field of 50 G.

In summary, we have developed a simple but effective solution-phase process for the fabrication of magnetically responsive photonic nanochains, each of which is composed of an array of magnetic $Fe_3O_4$ particles fixed within a silica shell. These photonic chains can be aligned in magnetic fields and diffract visible light. The key of the fabrication process is to induce chaining of the uniform magnetic particles during their silica coating process and then allow additional deposited silica to wrap entire chains into mechanically robust rods/wires. The diffraction wavelength of these photonic chains can be tailored across the visible spectrum by using magnetic particles of different sizes. The interparticle separation and the chain length can also be conveniently controlled by adjusting the timing and duration of applied magnetic field, respectively. The convenient control over the chain structure, nanoscale size of each diffracting unit, fast on/off switching of the diffraction state in response to external fields, tolerance to environmental variances, and excellent mechanical and optical stability make these photonic nanochains promising for many potential applications such as bio- and chemical sensing, labeling, and energy-efficient color displays.

## Experimental Section

Superparamagnetic $Fe_3O_4$ CNCs were synthesized using a high-temperature hydrolysis reaction that we reported previously.[4c] In a typical synthesis of photonic chains, an aqueous solution of CNCs (3 mL, ca. 8.6 mg $Fe_3O_4$/1 mL $H_2O$) was dispersed in a mixture of $NH_4OH$ (1 mL) and ethanol (20 mL) under sonication. After the mixture was transferred into a three-neck flask under mechanical stirring at 600 rpm, TEOS (170 μL) was quickly injected. After 12 min, 2 mL of the mixture was transferred to a glass vial (23 × 85 mm) and placed above a 75 × 6 mm neodymium disc magnet at a distance of 4 cm for 1 s. After removal from the magnetic field, the sample was allowed to sit undisturbed for another 15 min, after which it was washed with ethanol three times and redispersed in ethanol (4 mL).

The diffraction spectra were measured by an Ocean Optics HR 2000CG-UV-NIR spectrometer coupled with a six-around-one reflection/backscattering probe. The spectra integration time of collecting the signals was set to 500 ms.

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[1] a) J. D. Joannopoulos, R. D. Meade, J. N. Winn, *Photonic Crystals*, Princeton University Press, Princeton, **1995**; b) D. J. Norris, *Nat. Mater.* **2007**, *6*, 177–178; c) J. Ge, Y. Yin, *Angew. Chem.* **2011**, *123*, 1530–1561; *Angew. Chem. Int. Ed.* **2011**, *50*, 1492–1522.

[2] a) F. Fleischhaker, A. C. Arsenault, Z. Wang, V. Kitaev, F. C. Peiris, G. von Freymann, I. Manners, R. Zentel, G. A. Ozin, *Adv. Mater.* **2005**, *17*, 2455–2458; b) Z. Z. Gu, A. Fujishima, O. Sato, *J. Am. Chem. Soc.* **2000**, *122*, 12387–12388; c) O. D. Velev, A. M. Lenhoff, E. W. Kaler, *Science* **2000**, *287*, 2240–2243.

[3] a) R. A. Barry, P. Wiltzius, *Langmuir* **2006**, *22*, 1369–1374; b) F. Fleischhaker, A. C. Arsenault, V. Kitaev, F. C. Peiris, G. von Freymann, I. Manners, R. Zentel, G. A. Ozin, *J. Am. Chem. Soc.* **2005**, *127*, 9318–9319; c) S. A. Asher, V. L. Alexeev, A. V. Goponenko, A. C. Sharma, I. K. Lednev, C. S. Wilcox, D. N. Finegold, *J. Am. Chem. Soc.* **2003**, *125*, 3322–3329.

[4] a) J. Ge, Y. Yin, *J. Mater. Chem.* **2008**, *18*, 5041–5045; b) J. Ge, Y. Hu, T. Zhang, T. Huynh, Y. Yin, *Langmuir* **2008**, *24*, 3671–3680; c) J. Ge, Y. Hu, M. Biasini, W. P. Beyermann, Y. Yin, *Angew. Chem.* **2007**, *119*, 4420–4423; *Angew. Chem. Int. Ed.* **2007**, *46*, 4342–4345; d) J. Ge, Y. Hu, Y. Yin, *Angew. Chem.* **2007**, *119*, 7572–7575; *Angew. Chem. Int. Ed.* **2007**, *46*, 7428–7431; e) J. Ge, S. Kwon, Y. Yin, *J. Mater. Chem.* **2010**, *20*, 5777–5784.

[5] J. Ge, H. Lee, L. He, J. Kim, Z. Lu, H. Kim, J. Goebl, S. Kwon, Y. Yin, *J. Am. Chem. Soc.* **2009**, *131*, 15687–15694.

[6] a) A.-H. Lu, E. L. Salabas, F. Schüth, *Angew. Chem.* **2007**, *119*, 1242–1266; *Angew. Chem. Int. Ed.* **2007**, *46*, 1222–1244; b) M. Ye, Q. Zhang, Y. Hu, J. Ge, Z. Lu, L. He, Z. Chen, Y. Yin, *Chem. Eur. J.* **2010**, *16*, 6243–6250; c) R. Weissleder, H. C. Cheng, A. Bogdanova, A. Bogdanov, *J. Magn. Reson. Imaging* **1997**, *7*, 258–263; d) C. E. Reese, S. A. Asher, *Anal. Chem.* **2003**, *75*, 3915–3918.

[7] J. Ge, Y. Yin, *Adv. Mater.* **2008**, *20*, 3485–3491.

[8] J. Z. Wang, A. Sugawara, A. Shimojima, T. Okubo, *Langmuir* **2010**, *26*, 18491–18498.

[9] a) W. Y. Li, P. H. C. Camargo, L. Au, Q. Zhang, M. Rycenga, Y. N. Xia, *Angew. Chem.* **2010**, *122*, 168–172; *Angew. Chem. Int. Ed.* **2010**, *49*, 164–168; b) M. Ibisate, Z. Q. Zou, Y. N. Xia, *Adv. Funct. Mater.* **2006**, *16*, 1627–1632.

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