Assembly of Magnetically Tunable Photonic Crystals in Nonpolar Solvents

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Field-responsive photonic structures have important applications in areas such as color display units, biological and chemical sensors, and active optical components.[1−11] We have recently demonstrated a magnetically tunable photonic crystal system through the assembly of superparamagnetic iron oxide colloidal particles in aqueous solutions.[12,13] It has been realized that the key to a successful assembly and large tunability in photonic property is establishing long-range repulsive and attractive interactions that can cooperate to order the particles into periodic structures.[14] In the case of superparamagnetic iron oxide particles in aqueous solution, external magnetic fields induce strong attractive forces between neighboring magnetic particles along the field, bringing them close to each other. Electrostatic repulsive forces are introduced to the particles by coating them with a layer of polyelectrolytes containing high density negative charges. The two forces reach a balance, eventually organizing the particles into long chains with equal interparticle separations. Diffraction occurs when the periodicity of the as-sembled structure and the wavelength of the incident light satisfy the Bragg condition.[15,16] A variation in the strength of the magnetic field changes the strength of the attractive force, consequently the interparticle separation, and eventually the diffraction wavelength. The advantages of such a system include a wide tuning range covering the entire visible spectrum, a fast and fully reversible response, and the compatibility with miniaturization for device fabrication.

Practical applications often require the use of nonaqueous solvents to achieve long-term stability and improved compatibility with device fabrication processes. Besides particle dispersibility, the major challenge involved in building tunable photonic crystals is the establishment of sufficiently strong and long-range repulsive forces to balance the magnetic attractive force because the electrostatic forces are usually greatly diminished in nonaqueous solvents. We have recently extended the assembly process to alkanol solvents by making use of the long-range electrostatic force and the short-range solvation force, the latter of which is originated from the overlap of two relatively thick solvation layers on the hydrophilic silica covered particle surfaces.[17] However, it has been a great challenge to establish long-range electrostatic repulsive interactions in nonpolar solvents because the energy barrier to forming surface charges is ∼40 times larger than that in water. The solvation force between two hydrophobic surfaces in a nonpolar solvent is also negligible because of the extremely thin solvation layers. In this communication, we address the above challenge by introducing charge control agents in nonpolar solvents to reduce the energy barrier of charge separation, and thus creating long-range electrostatic repulsive interactions that can counteract the magnetic attraction to allow ordering of superparamagnetic colloids.

We first improve the dispersibility of the iron oxide particles in nonpolar solvents through surface modification by taking advantage of well-developed silane chemistry.[18,19] In a typical process, uniform superparamagnetic Fe_3O_4 colloidal particles with an average diameter of ∼163 nm are first synthesized using a previously
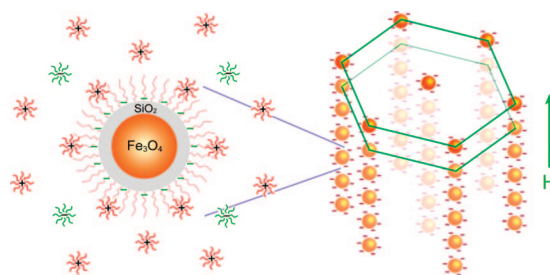

Figure 1. Schematic illustrations showing the creation of negative charges on the surface of superparamagnetic colloids in nonpolar solvents by introducing charge control agent AOT (left), and the assembly of such charged particles into tunable photonic structures upon application of an external magnetic field (right).

reported procedure[20] and then coated with a thin layer of silica by using a modified Stöber process.[17,21] The Fe_3O_4@SiO_2 particles are dried in air and then transferred to a solution of *n*-octadecyl-trimethoxysilane (ODTMS) in 1,2-dichlorobenzene (DCB). The mixture is stirred at 120 °C for 3 h to allow the hydrolyzable alkoxy groups of the organosilanes to attack the surface silanols through an alcoholysis reaction. As a result, a monolayer of hydrophobic alkyl chains is grafted to the silica surface through the covalent −Si−O−Si− bonds, making the particles dispersible in most nonpolar solvents such as 1,2-dichlorobenzene, toluene, chloroform, and hexane.

Both the degree of grafting (disappearance of hydrophilic silanols) and the shielding ability of grafted hydrophobic chains contribute to the dispersibility of the modified Fe_3O_4@SiO_2 particles in nonpolar solvents. Typically, long reaction time (>3 h) and the use of small alkoxy groups, such as methoxy groups which are reactive even without catalyst, favor a high degree of grafting. On the other hand, organosilanes with long alkyl chains are preferred because they can effectively shield the unreacted silanol groups.[18] Among many organosilanes we have tested, ODTMS provides the best dispersibility because it contains small alkoxy groups and a relatively long alkyl chain.

Direct assembly of surface-modified particles in nonpolar solvents, such as toluene and hexane, was difficult because of the lack of strong and long-range repulsive forces to balance the magnetic attractive force. It is known that the thermodynamics of charging in a liquid is controlled by the Bjerrum length, which is the characteristic separation between two ions at which their Coulombic interactions are exactly balanced by the thermal energy.[22] Since nonpolar solvents usually have much lower dielectric constants and much higher Bjerrum lengths than those of polar solvents, charge separation is extremely difficult and energetically expensive, leading to a common expectation that electrostatic repulsion is negligible in nonpolar solvents.[22−27] However, it has been reported that the addition of charge control agents or surfactants to nonpolar dispersions can produce small reverse micelles of a few nanometers in diameter, which reduce
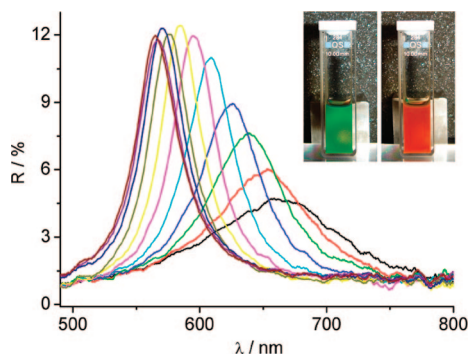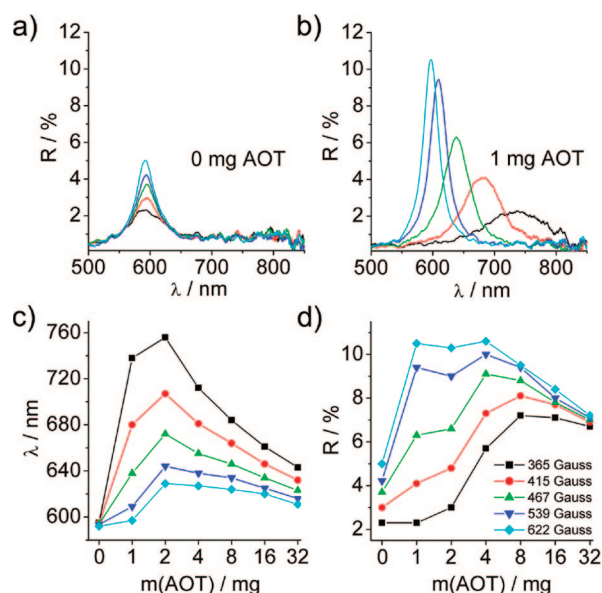
Figure 2. Reflection spectra of a DCB solution of 163-nm (115/24-nm) $Fe_3O_4@SiO_2$ particles in response to an external magnetic field with varying strengths achieved by changing the magnet−sample distance. Diffraction peaks blue shift as the distance decreases from 4.3 to 2.3 cm with a step size of 0.2 cm. Inset shows the digital photo of the DCB solution diffracting green and red lights under magnetic fields with two different strengths.

the energy barrier of charge separation and enhance surface charges by stabilizing their counterions in the cores of micelles.[25−27] Due to the inevitable trace amount of water in the system, the amphiphilic molecules form reverse micelles with a hydrophilic aqueous core available for solvation of ions.[26] Because of the practically low concentration of charge carriers in a nonpolar solvent, screening of electrostatic interactions is low and charge interactions are extremely long-ranged. As a result, strong electrostatic repulsions with screening length κ^{-1} from 0.2 to 1.4 μm can be achieved by simply introducing charge control agents. In addition, a small fraction of micelles spontaneously ionizes as the result of thermal fluctuations to contribute to the screening of particle interactions on longer length scales.[22] Thus, upon the addition of reverse micelles, the charge behavior of a nonpolar dispersion comes to mimic that of an aqueous system in many ways (Figure 1).[25] For example, electrostatic interactions have the same functional form as those predicted from the classic theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) for polar liquids, so that the charge behavior can be described in a way similar to the double layer model.[28,29] Additionally, particle surface potentials are remarkably large, comparable to those of highly charged aqueous colloids.[25] It is therefore expected that the long-range electrostatic repulsions induced by the charge control agents can counterbalance the magnetic attraction to assemble superparamagnetic colloids in nonpolar solvents.

We choose sodium bis(2-ethylhexyl) sulfosuccinate (AOT), a typical ionic surfactant, as the charge control agent. The ODTMS modified $Fe_3O_4@SiO_2$ colloids remain a good dispersion in most nonpolar solvents upon addition of AOT. To qualitatively characterize the induced surface charges, we performed a simple electrophoresis experiment by applying a voltage (280 V) across a DCB solution containing both particles and AOT through two immersed stainless steel electrodes (Figure S2). After ∼10 min, a brownish deposition of $Fe_3O_4@SiO_2$ particles appeared on the anode, while the cathode remained clean. This experiment not only confirms the enhanced charge separation by addition of the charge control agent AOT but also demonstrates that the silica surfaces are negatively charged.

The successful establishment of long-range electrostatic repulsive interactions makes it possible to assemble the superparamagnetic colloids into tunable photonic crystals in nonpolar solvents by balancing the attractive force induced by external magnetic fields. Compared to the cases in aqueous and alkanol solutions, the current system retains the fast and fully reversible optical response to the external fields, long-term stability (>half-year), and reasonably

strong diffraction intensity. Figure 2 shows the typical reflection spectra of $Fe_3O_4@SiO_2$ photonic crystals in DCB in response to a varying magnetic field, which is achieved by changing the distance between the magnet and the sample. The diffraction peak blue-shifts from 665 to 564 nm as the magnetic field increases from 191 to 622 gauss. Similar to the aqueous case, the tuning of the diffraction is realized through automatic adjustment of interparticle distance, which is required to change the strength of electrostatic repulsion to reach a balance with the varying magnetic attractive force. The contour of the diffraction peaks shows a skewed profile as the magnetic field is tuned, which is similar to that in the alkanol case and implies the existence of structural repulsion in the short-range in addition to the long-range electrostatic force.[17] The typical tuning range of the photonic crystals in nonpolar solvents is within ∼150 nm, which, unlike the aqueous system, can not cover the entire visible spectrum. If needed, $Fe_3O_4@SiO_2$ building blocks with different sizes can be assembled to display various colors, such as blue-green (Figure S3), green-red (Figure 2), and red-infrared (Figure S4).

Figure 3. (a, b) Reflection spectra of a 1.5 mL DCB solution containing 167-nm (103/32-nm) $Fe_3O_4@SiO_2$ particles and (a) 0 mg and (b) 1 mg of AOT in response to an external magnetic field with varying strengths, respectively. (c, d) Dependence of (c) diffraction wavelength and (d) intensity upon the AOT concentration in magnetic fields with five different strengths.

The charge control agent AOT plays an important role in controlling the assembly behavior of superparamagnetic colloidal particles. In a DCB solution without AOT, as shown in Figure 3a, the hydrophobic $Fe_3O_4@SiO_2$ colloids can self-assemble into ordered structures whose diffraction intensity increases slightly in an enhancing external magnetic field. However, the diffraction peaks remain at a fixed wavelength, suggesting a lack of strong long-range repulsive forces. The colloidal particles behave like hard spheres so that strong repulsion only appears when they are close to contact, making it impossible to tune the particle separation. When AOT is added in the same solution, considerable negative charges build up on the particle surface due to the enhanced charge separation. The particles interact with each other through the long-range electrostatic forces which dynamically balance the magnetic attraction and assemble them into chains with tunable particle separation. As shown in Figure 3b, the diffraction peaks red-shift

and can be tuned within a range of ~150 nm by varying the strength of the external magnetic field.

The small AOT micelles are believed to serve two functions in determining the strength of electrostatic interactions. On one hand, the micelles provide a polar environment for the surface ions, which are originally hard to separate from the colloids in pure nonpolar solvents. Since micelles can exchange their inner contents through collision, the ions can be carried into the bulk solution, leaving behind a net charged colloid surface.[25,26] On the other hand, the AOT molecules can also dissociate to Na^+ and counterions, which are then separated by the micelle exchange, leading to the formation of charged micelles. Similar to the ions in aqueous colloidal systems, these charged micelles may screen the electrostatic interactions in nonpolar solvents (Figure 1).

The two functions can be clearly observed by studying the dependence of the diffraction wavelength on the concentration of AOT. We recorded a series of diffraction spectra of systems containing different concentrations of AOT in response to external magnetic fields (Figure S5). The data are replotted in Figure 3C to highlight the dependence of the diffraction wavelength on the AOT concentration at fixed magnetic fields. Apparently, the primary effect of AOT at low concentrations is to induce charge separation on the particle surface, as evidenced by the significant red shift of the diffraction peaks. When the red shift reaches maximum, further increase of the concentration of AOT creates free charged micelles which screen the electrostatic interactions between particles in a way analogous to the increase of ionic strength in aqueous solutions.[13] As a result, the tuning range of the diffraction, as represented by the difference between the black and sky blue point at each concentration, shrinks upon further addition of AOT.[13] Accordingly, as shown in Figure 3D, the maximum diffraction intensity can be reached when the concentration of the AOT increases to the intermediate values. Additional AOT will decrease the diffraction intensity which is again consistent with the case of adding salt to aqueous solution. It is worth noting that, even with screening from the charged micelles, the overall diffraction intensity is still significantly higher than the case without AOT.

In summary, we have successfully established long-range electrostatic repulsive forces in nonpolar solvents to allow the assembly of superparamagnetic colloids into ordered structures with magnetically tunable photonic properties. The introduction of charge control agents such as AOT molecules produces micelles which can enhance the charge separation on the surfaces of ODTMS modified $Fe_3O_4@SiO_2$ particles. The significantly improved long-range electrostatic repulsion can balance the magnetically induced attraction and therefore allow ordering of superparamagnetic colloids in nonpolar solvents. This system possesses a fast and fully reversible optical response to the external magnetic field, long-term stability in performance, and good diffraction intensity. Besides the potential technological applications utilizing the field-responsive photonic properties, this work may also provide a convenient, quantitative optical method for studying fundamental topics such as the mechanism of charging in solvents of low permittivity.

Supporting Information Available: Experimental procedures, TEM images, electrophoresis experiment, diffraction evolution of $Fe_3O_4@SiO_2$ colloids of various sizes in DCB in a strength changing magnetic field, and diffraction of several nonpolar systems. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Fudouzi, H.; Xia, Y. Langmuir 2003, 19, 9653–9660.
(2) Asher, S. A.; Sharma, A. C.; Goponenko, A. V.; Ward, M. M. Anal. Chem. 2003, 75, 1676–1683.
(3) Lawrence, J. R.; Ying, Y.; Jiang, P.; Foulger, S. H. Adv. Mater. 2006, 18, 300–303.
(4) Tian, E.; Wang, J.; Zheng, Y.; Song, Y.; Jiang, L.; Zhu, D. J. Mater. Chem. 2008, 18, 1116–1122.
(5) Arsenault, A. C.; Puzzo, D. P.; Manners, I.; Ozin, G. A. Nat. Photon. 2007, 1, 468–472.
(6) Gu, Z. Z.; Fujishima, A.; Sato, O. J. Am. Chem. Soc. 2000, 122, 12387–12388.
(7) Sumioka, K.; Kayashima, H.; Tsutsui, T. Adv. Mater. 2002, 14, 1284–1286.
(8) Jeong, U.; Xia, Y. Angew. Chem., Int. Ed. 2005, 44, 3099–3103.
(9) Kuai, S.-L.; Bader, G.; Ashrit, P. V. Appl. Phys. Lett. 2005, 86, 221110.
(10) Lumsdon, S. O.; Kaler, E. W.; Williams, J. P.; Velev, O. D. Appl. Phys. Lett. 2003, 82, 949–951.
(11) Mach, P.; Wiltzius, P.; Megens, M.; Weitz, D. A.; Lin, K.-h.; Lubensky, T. C.; Yodh, A. G. J. Europhys. Lett. 2002, 58, 679–685.
(12) Ge, J.; Hu, Y.; Yin, Y. Angew. Chem., Int. Ed. 2007, 46, 7428–7431.
(13) Ge, J.; Hu, Y.; Zhang, T.; Huynh, T.; Yin, Y. Langmuir 2008, 24, 3671–3680.
(14) Ge, J.; Yin, Y. J. Mater. Chem. 2008, 18, 5041–5045.
(15) Bibette, J. J. Magn. Magn. Mater. 1993, 122, 37–41.
(16) Calderon, F. L.; Stora, T.; Mondain Monval, O.; Poulin, P.; Bibette, J. Phys. Rev. Lett. 1994, 72, 2959–2962.
(17) Ge, J.; Yin, Y. Adv. Mater. 2008, 20, 3485–3491.
(18) Garcia, N.; Benito, E.; Guzman, J.; Tiemblo, P. J. Am. Chem. Soc. 2007, 129, 5052–5060.
(19) Wang, W.; Gu, B. H.; Liang, L. Y.; Hamilton, W. J. Phys. Chem. B 2003, 107, 3400–3404.
(20) Ge, J.; Hu, Y.; Biasini, M.; Beyermann, W. P.; Yin, Y. Angew. Chem., Int. Ed. 2007, 46, 4342–4345.
(21) Ge, J.; Hu, Y.; Zhang, T.; Yin, Y. J. Am. Chem. Soc. 2007, 129, 8974–8975.
(22) Roberts, G. S.; Sanchez, R.; Kemp, R.; Wood, T.; Bartlett, P. Langmuir 2008, 24, 6530–6541.
(23) Chen, Y.; Au, J.; Kazlas, P.; Ritenour, A.; Gates, H.; McCreary, M. Nature 2003, 423, 136–136.
(24) Comiskey, B.; Albert, J. D.; Yoshizawa, H.; Jacobson, J. Nature 1998, 394, 253–255.
(25) Hsu, M. F.; Dufresne, E. R.; Weitz, D. A. Langmuir 2005, 21, 4881–4887.
(26) Briscoe, W. H.; Horn, R. G. Langmuir 2002, 18, 3945–3956.
(27) Sainis, S. K.; Germain, V.; Mejean, C. O.; Dufresne, E. R. Langmuir 2008, 24, 1160–1164.
(28) Derjaguin, B. V.; Landau, L. Acta Physicochimica (USSR) 1941, 14, 633–662.
(29) Verwey, E. J. W.; Overbeek, J. T. G. Theory of Stability of Lyophobic Colloids; Elsevier: Amsterdam, 1948.

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