



Magnetic Assembly and Field-Tuning of Ellipsoidal-Nanoparticle-Based Colloidal Photonic Crystals**

Mingsheng Wang, Le He, Wenjing Xu, Xin Wang, and Yadong Yin*

Abstract: Anisotropic nanostructures provide an additional degree of freedom for tailoring the collective properties of their ensembles. Using Fe@SiO₂ nanoellipsoids as anisotropic building blocks, herein we demonstrate a new class of magnetically responsive photonic structures whose photonic properties can be dynamically tuned by controlling the direction of the magnetic fields they are exposed to. These novel photonic structures diffract at a minimum wavelength when the field direction is perpendicular to the incident angle, and a maximum wavelength when the field is switched to parallel direction; and the diffraction intensity reaches maximum values when the fields are either parallel or perpendicular to the incident light, and decreases when the field direction is moved off-angle.

Colloidal assembly has been widely explored to produce artificial structural color by manipulating the light interaction with physical periodic structures.^[1] Easily found in nature, such as opals, bird feathers, and butterfly scales, structural color is brilliantly iridescent, metallic, and free from photobleaching unlike conventional pigments or dyes. Most colloidal assembly processes mimic the formation of opals and create close-packed structures from monodisperse colloidal spheres. However, living systems often involve non-close-packed ordered assemblies of anisotropic motifs, such as plates and rods, thus display significantly more complex structural color responses including strong angular dependence and polarization effect.^[2] Prior efforts have been made to organizing elongated particles, such as polystyrene and ZnS,^[3] albeit the assembly methods are rather conventional and the resulting crystals do not exhibit different photonic responses to those from spherical particles.

One of the important advantages of anisotropic particles is that they often have shape-dependent physical and chemical properties, which can add more degrees of freedom for manipulating the collective properties of the resultant superstructures. This is of particular interest to the fabrication of field-responsive colloidal photonic structures, in which static or dynamic structural changes are usually accompanied

by switching of photonic properties.^[4] Efforts along this direction, however, have been very limited, mostly owing to the unavailability of high-quality anisotropic building blocks and the lack of effective mechanism for assembly and tuning. Herein we report the synthesis of well-defined ellipsoidal colloidal particles with anisotropy in both morphology and magnetic properties and then demonstrate their assembly into three-dimensional ordered structures with unique tunable photonic properties. Unlike conventional colloidal crystals made from spherical magnetic particles where dynamic tuning of photonic property can only be achieved by controlling the field strength,^[4a,5] the diffraction properties of the current systems are strongly dependent on the field direction, which affects the orientation of the ellipsoidal particles. A wide range of tuning in the diffraction spectrum can therefore be achieved by controlling the direction of the external magnetic field, while the field strength has only minimal influence on the diffraction wavelength.

As uniform magnetic ellipsoidal particles are not directly available, we took an indirect approach by first synthesizing uniform iron oxyhydroxide (FeOOH) nanorods,^[6] then coating them with silica to form composite ellipsoids, and finally converting the FeOOH into magnetic metallic iron through reduction. Figure 1a,b show TEM images of two typical samples of FeOOH nanorods with average dimensions of 70 nm × 10 nm (length × diameter, FeOOH-A) and 110 nm × 20 nm (FeOOH-B). The surface of as-prepared FeOOH nanorods were functionalized by polyacrylic acid, and coated with a thick layer of silica. During the coating process, the aspect ratio of nanorods decreased and eventually led to the formation of ellipsoids. To convert the FeOOH core into magnetic species, the FeOOH@SiO₂ ellipsoids were reduced in H₂ at 500 °C.^[7] Figure 1c,d show the TEM images of as-reduced samples, clearly indicating a uniform ellipsoidal morphology. The nanoellipsoids synthesized from FeOOH-A (NE-A) have an average dimension of 190 nm × 130 nm and those from FeOOH-B (NE-B) of 220 nm × 130 nm. X-ray diffraction (XRD) measurements indicate that the reduction results in the formation of metallic iron (Figure S1 in the Supporting Information). Magnetic characterizations in Figure 1e,f confirm the ferromagnetic property of the reduced samples, showing a saturated magnetization of 0.6 emu g⁻¹ and a coercivity of 500 G for NE-A, and a saturated magnetization of 1.2 emu g⁻¹ and a coercivity of 800 G for NE-B. The magnetizations of NE-A and NE-B are about two orders of magnitude smaller than the superparamagnetic colloidal nanocrystal clusters that were used to construct one-dimensional photonic chains in our previous work.^[4a] As the magnetic dipole-dipole interactions between nanoellipsoids are negligible, they do not show any apparent sign of

[*] M. Wang, Dr. L. He, W. Xu, X. Wang, Prof. Y. Yin
Department of Chemistry
University of California, Riverside
Riverside, CA 92521 (USA)
E-mail: yadong.yin@ucr.edu

[**] This work was partially supported by the U. S. Army Research Laboratory (W911NF-10-1-0484) and U. S. National Science Foundation (DMR-0956081).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201501782>.

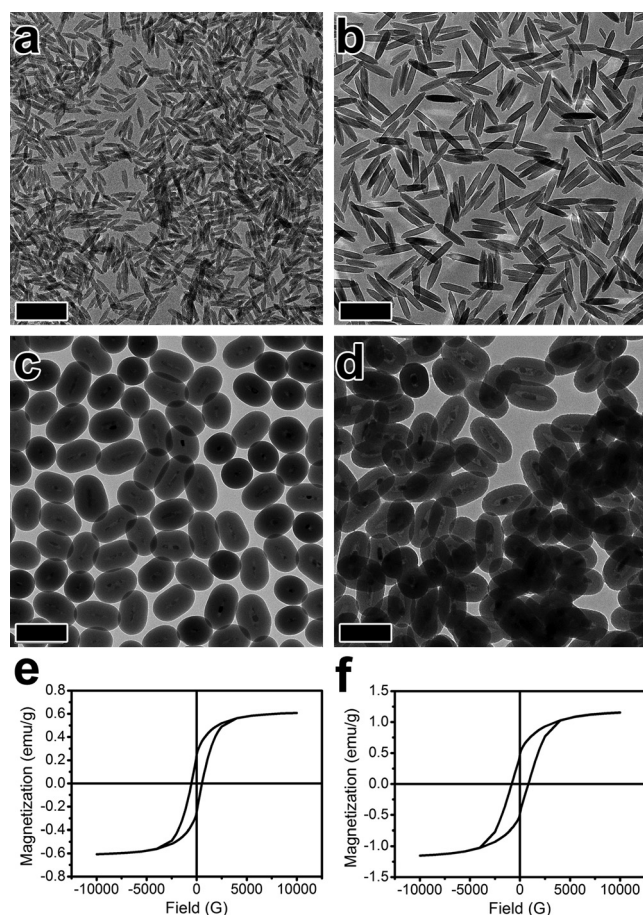


Figure 1. a,b) TEM images of two typical samples of FeOOH nanorods denoted as A and B, respectively; c,d) TEM images of magnetic nanoellipsoids obtained by coating these FeOOH nanorods with silica and then reducing them with H_2 ; e,f) the corresponding magnetic hysteresis loops of the nanoellipsoids. Results in panels (c,e) correspond to samples of NE-A and in (d,f) to NE-B. All scale bars: 200 nm.

aggregation/assembly when exposed to external magnetic fields, as demonstrated in Figure S2.

The silica coating plays multiple important roles in this system. First, it increases the dimensions of the FeOOH nanorods to the size range suitable for creating photonic responses in the visible spectrum. Second, it provides a protection mechanism that prevents the disintegration of the nanorods during the conversion from FeOOH into Fe which involves dehydration and reduction reactions and consequently significant morphological changes. Finally, the silica layer acts as a spacer that separates the magnetic nanorods by certain distance and limits their mutual magnetic attraction, therefore preventing their colloidal dispersion from aggregation despite the ferromagnetic nature of the nanorods.

An additional benefit of having the silica layer is the ease of establishing electrostatic interactions among the ellipsoids, which is the key for the successful assembly of colloids photonic crystals.^[8] The as-reduced nanoellipsoidal particles, although dispersible in water, do not possess sufficient charge on their surfaces to establish electrostatic interactions, as

confirmed by ζ -potential measurements. However, this issue can be conveniently addressed by heating the ellipsoids in water under reflux, during which more silanol groups are created on the particle surface by etching of the silica layer by water. A concentrated solution of such highly charged particles can self-assemble into ordered structures even without the presence of external fields, as driven by minimization of electrostatic repulsive interactions.^[1d,5b,8,9] An external magnetic field, however, can help to align the ellipsoids, decrease ordering defects, and improve the reflectance of the colloidal assemblies.

By using NE-A as an example, we demonstrate (Figure 2) the effect of reflux in water on the surface charge of the ellipsoids and the diffraction intensity of the resultant

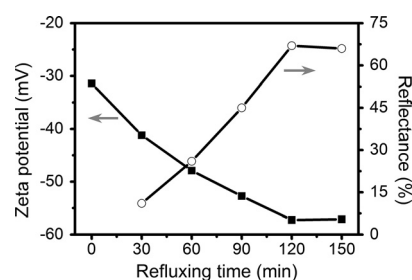


Figure 2. Dependence of zeta potential on time under reflux for nanoellipsoids of NE-A, and the corresponding reflectance intensity of colloidal photonic crystals assembled under a magnetic field with direction perpendicular to incident angle.

photonic crystals. A magnetic field of approximately 50 mT was applied perpendicular to the direction of incident light to improve ordering during the measurement. The ζ -potential of as-reduced nanoparticles was found to be -31 mV, which was insufficient to ensure long-range order in a concentrated solution, as confirmed by the poor photonic performance measured in the reflectance mode. Refluxing the nanoellipsoids in water significantly enhanced the surface charges as well as their photonic performance. After 2 h under reflux, the ζ -potential dropped to -57 mV, comparable to the polyacrylate-capped Fe_3O_4 particles (-49 mV) and the refluxed $Fe_3O_4@SiO_2$ particles (-56.5 mV) that we reported before,^[4b,5b] and thus dramatically enhanced the reflectance intensity (ca. 67.5%). Since extending the refluxing time to 150 min led to almost the same results, we used samples that had been under reflux for 2 h for all the following measurements and discussions.

Compared with spheres, a unique feature of the anisotropic nanoellipsoids is that their photonic assemblies show a strong dependence to field direction. In addition to the positional order that is usually considered for describing assemblies from spherical building blocks, orientational order should also be taken into account when nanoellipsoids are assembled.^[10] Upon the application of magnetic fields, nanoellipsoids rotate and align their long axis parallel to the field direction (Figure 3a). Such rotation not only gives rise to changes in orientational orders, but also affects positional orders and subsequently photonic properties of the assemblies. In addition, the field strength also plays an important

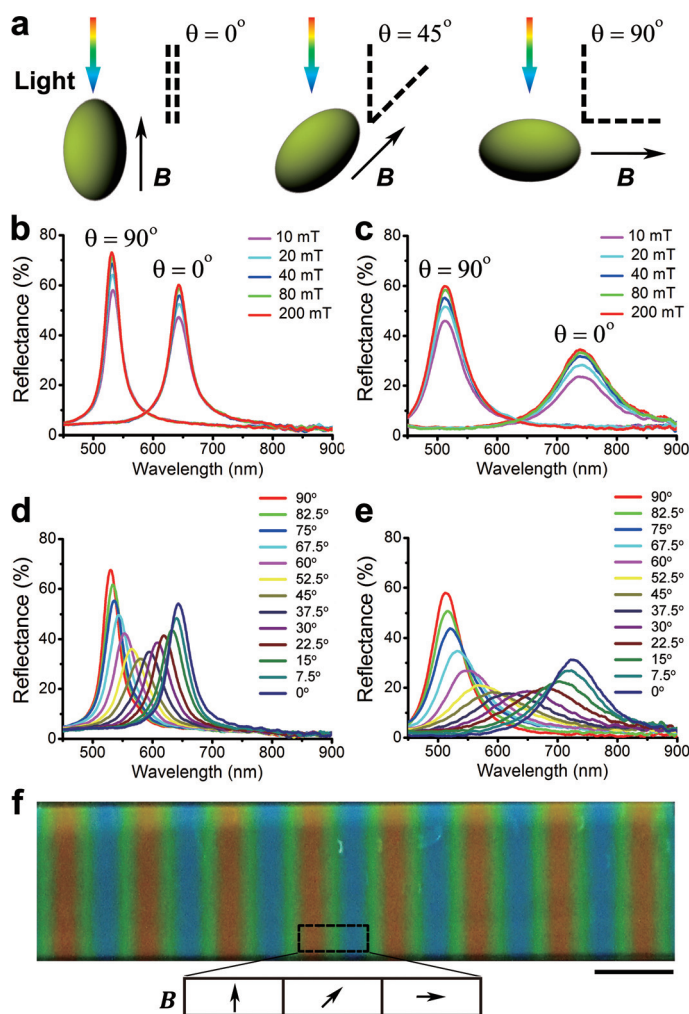


Figure 3. a) Schematic representation of the spontaneous alignment of nanoellipsoids under magnetic fields; b,c) Reflection spectra of photonic structures under perpendicular and parallel magnetic fields with varying strengths; d,e) Reflection spectra of photonic structures under magnetic fields with varying directions with respect to the direction of light. Results in (b,d) are for NE-A, those in (c,e) are for NE-B. f) Digital photo showing the photonic response of NE-B encapsulated in a flat glass tube under a non-ideal linear Halbach array. The scale bar corresponds to 5 mm.

role in the perfection of ordering since it determines to what degree the nanoellipsoids can align.

To investigate the effect of field strength and direction, we examined the photonic properties of structures assembled from samples of NE-A and NE-B, under magnetic fields with varying strengths and directions. Aqueous dispersions of nanoellipsoids were concentrated to a volume fraction of 18% to allow their spontaneous ordering into colloidal crystals. Figure 3b,c show the reflection spectra of photonic structures assembled from these two samples under magnetic fields parallel and perpendicular to the incident light. A magnetic field perpendicular to the light aligns nanoellipsoids in the perpendicular orientation so that the interplanar spacing is mainly determined by the short axis of nanoellipsoids, resulting in a reflection peak at shorter wavelength. When the field direction is switched to be parallel to the light, the interplanar spacing is determined by the long axis of

nanoellipsoids, accounting for a reflection peak at longer wavelength. The field strength, on the other hand, is found to influence the intensity of reflectance rather than the wavelength, for both samples. The increased reflectance intensity under stronger fields is believed to result from the better orientational order of the nanoellipsoids: because of the limited amount of magnetic species embedded inside them, the rotation of nanoellipsoids requires a sufficiently high magnetic field to allow the magnetic torque to overcome the rotational resistance. When the field direction is fixed, varying the field strength does not alter the reflection wavelength. The contribution of the magnetic interactions between nanoellipsoids to the interplanar spacing of the assemblies seems to be negligible, mainly owing to the effective separation of the magnetic nanorods by the relatively thick silica coating.

Different from conventional colloidal crystals assembled using spheres where tuning of photonic property can only be achieved by controlling the interplanar spacing through variation in field strength,^[4a,5,11] tuning field direction results in simultaneous rotation of nanoellipsoids, which further leads to changes in the orientation of the crystal assemblies as well as their photonic properties.^[4b] We investigated the photonic property of structures assembled from NE-A and NE-B, under a rotating magnetic field of approximately 50 mT. As shown in Figure 3d,e, the wavelength of reflectance peak reaches a minimum value when the field direction is perpendicular to the incident light, and gradually red shifts as the field switches from perpendicular to parallel to the incident light. Such shift in reflection wavelengths responds to the change of field direction immediately (< 1 s) and is fully reversible. A notable feature of such magnetic tuning is that the maximum intensity is achieved at the two end points when the magnetic fields are either parallel or perpendicular to the incident light. When the field direction is switched away from these two end points, the relative intensity decreases and reaches a minimum at the middle point (ca. 45° from the parallel and perpendicular directions), resulting in an overall U-shaped profile of reflectance peaks. This is a major difference when compared to one-dimensional photonic chains where the strongest reflectance is only achievable under intermediate field intensity and the profile of reflectance peaks is an inverted U curve.^[4a] As expected, nanoellipsoids with higher aspect ratio, as in the case of NE-B than that of NE-A, lead to more changes in the interplanar spacing when the orientation of the assembled crystals are switched, resulting in a broader tuning range in photonic response.

The orientational dependence of the nanoellipsoidal assemblies can find direct use in creating photonic patterns under magnetic fields with non-uniform field directions. As demonstrated in Figure 3f, when subjected to complex magnetic field produced by a non-ideal linear Halbach array which has a spatially rotating pattern of magnetization, a dispersion of NE-B encapsulated in a flat glass tube exhibits a rainbow pattern containing blue, green, and red stripes. Unlike our previously demonstrated one-dimensional photonic assembly which only shows single color stripes at areas

with field parallel to the incident angle,^[5a] the current system displays red and blue stripes at areas with parallel and horizontal fields, and a transitional green stripe in between at off-angle areas.

In addition to orientation, the interplanar spacing of the photonic assemblies is also determined by the volume fractions of the nanoellipsoids.^[4b] As the volume fraction decreases, the distance between nanoellipsoids increases, resulting in the expansion of crystal lattice as well as red-shift of reflection wavelength. In the absence of magnetic fields, the reflection spectra of photonic assemblies formed by NE-A under different volume fractions were recorded (Figure 4a). The reflection peak shifted from 425 nm to 660 nm,

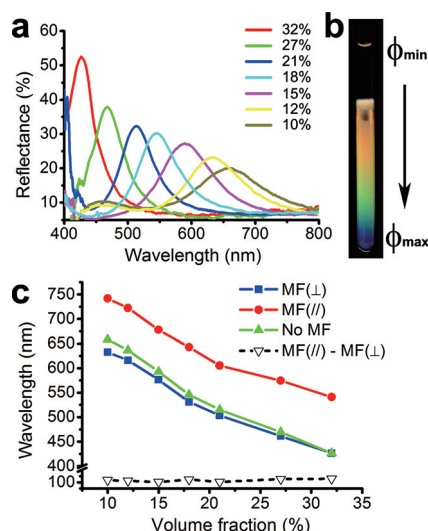


Figure 4. a) Reflection spectra of the colloidal dispersion of the NE-A under different volume fractions in the absence of magnetic fields; b) Digital image of the dispersion of the NE-A in a glass capillary tube with a volume fraction gradient; c) Dependence of reflection wavelength of photonic structures on the volume fraction of the NE-A, in the presence or absence of magnetic fields (MF).

as the volume fractions decreased from 32% to 10%. Consistently, a rainbow-like color effect was observed (Figure 4b) in the dispersion of NE-A with a volume fraction gradient, which was achieved by centrifugation at 3000 rpm for 5 min.

The synergy between field direction and volume fraction allows for a wide range of tuning of the optical property of the assemblies. Figure 4c plots the changes in peak positions with volume fraction of the solution for sample NE-A under parallel or perpendicular magnetic fields or no field. Interestingly, for each volume fraction, the difference in the peak position of the photonic assemblies under parallel and perpendicular magnetic fields remains constantly at around 105 nm, as represented by the black dashed line in Figure 4c. Such a difference in peak positions is attributed to the difference in the long axis and the short axis of nanoellipsoids, and therefore is not subjected to change with volume fraction. Without magnetic fields, the orientation of nanoellipsoids is less uniform so that the interplanar spacings of the assemblies and the positions of reflection peaks are always between those

under parallel and perpendicular fields. In the absence of external fields, the nanoellipsoids tend to align themselves along the surface of sample container, which is perpendicular to the incident angle so that the reflection peak is close to that of the case with a perpendicular field (Figure 4c). The orientational order of nanoellipsoids enhances as the volume fraction increases and eventually becomes nearly the same as the case aligned by magnetic fields, as confirmed by the coincidence of the peak positions at a high volume fraction of approximately 32%. The enhanced orientational order can be explained by the reduced excluded volume of each nanoellipsoid at a higher volume fraction.^[12]

Theoretical investigations have predicted that anisotropic nanoparticles would preferentially form a stretched face-centered cubic (*fcc*) structure as the volume fraction reaches a critical threshold.^[13] As illustrated in Figure 5a, when the

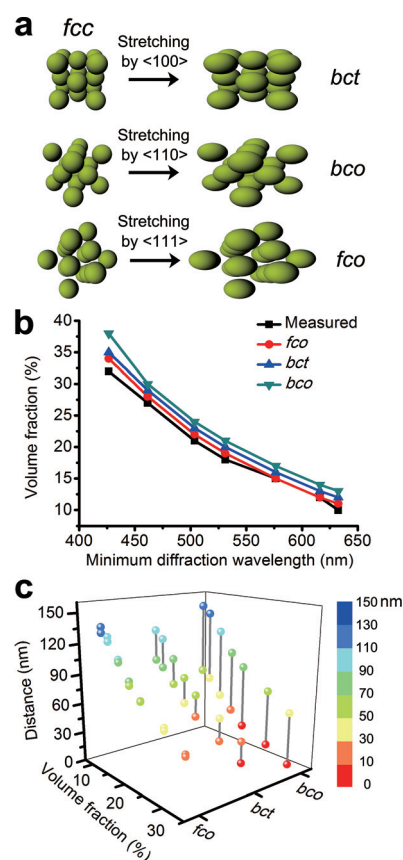


Figure 5. a) Possible structures resulting from the assembly of nanoellipsoids; b) The measured volume fractions to the calculated values for sample NE-A; c) Calculated surface-to-surface distances between one particular nanoellipsoid to its neighbors in the three possible structures.

original *fcc* lattice is stretched along $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 111 \rangle$ axes, it transforms into body-centered tetragonal (*bct*), body-centered orthorhombic (*bco*), or face-centered orthorhombic (*fco*) lattices, respectively. The periodicities of photonic assemblies along different axes were calculated using diffraction wavelengths through Bragg's law; they were then plugged in the above three lattices to find out the lattice constants. As

shown in Figure 5b, the *fco* lattice has the closest value to the experimental volume fractions compared to the *bct* and *bco* lattices. In the *fco* lattice, the distances between one particular ellipsoid and its twelve nearest neighbors are almost identical; while in the *bct* or *bco* lattices, the interparticle distances vary more than 30 nm or 60 nm, respectively, as plotted in Figure 5c. As the assembly of nanoellipsoids is driven solely by electrostatic forces, the interparticle surface-to-surface distances are not expected to vary significantly. Therefore in our system, nanoellipsoids were most likely assembled into an *fco* lattice, in accordance to theoretical predictions that the *fco* lattice is most energetically favorable among the above three structures.^[14]

In summary, we have demonstrated a new class of magnetically responsive photonic crystals whose diffraction properties can be widely tuned instantaneously and fully reversibly by controlling the field direction. Assembled from uniform shape- and magnetically anisotropic nanoellipsoidal particles, the novel colloidal crystals diffract at a minimum wavelength when the field direction is perpendicular to the incident angle and a maximum wavelength when the field is switched to parallel. The diffraction intensity reaches maximum values when the field is either parallel or perpendicular to the incident light, and decreases when the field direction is off-angle, displaying a unique U-shaped profile in reflectance peaks. The current system not only allows more opportunities in studying the assembly behavior of shape- and magnetically anisotropic nanostructures but also provides a new platform for building novel active optical components for various color presentation and display applications.

Keywords: anisotropic nanomaterials · magnetic properties · photonic structures · self-assembly

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7077–7081
Angew. Chem. **2015**, *127*, 7183–7187

- [1] a) Y. Xia, B. Gates, Z. Li, *Adv. Mater.* **2001**, *13*, 409–413; b) A. K. Boal, F. Ilhan, J. E. DeRouchey, T. Thurn-Albrecht, T. P. Russell, V. M. Rotello, *Nature* **2000**, *404*, 746–748; c) M. Li, H. Schnablegger, S. Mann, *Nature* **1999**, *402*, 393–395; d) G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418–2421.
- [2] a) C. Lawrence, P. Vukusic, R. Sambles, *Appl. Opt.* **2002**, *41*, 437–441; b) N. Okada, D. Zhu, D. Cai, J. Cole, M. Kambe, S. Kinoshita, *J. Opt.* **2013**, *42*, 25–36; c) P. Vukusic, J. R. Sambles, C. R. Lawrence, R. J. Wootton, *Nature* **2001**, *410*, 36; d) S. Vignolini, P. J. Rudall, A. V. Rowland, A. Reed, E. Moyroud, R. B. Faden, J. J. Baumberg, B. J. Glover, U. Steiner, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15712–15715; e) D. G. Stavenga, B. D. Wilts, H. L. Leertouwer, T. Hariyama, *Philos. Trans. R. Soc. London Ser. B* **2011**, *366*, 709–723; f) V. Sharma, M. Crne, J. O. Park, M. Srinivasarao, *Science* **2009**, *325*, 449–451.
- [3] a) J. D. Forster, J. G. Park, M. Mittal, H. Noh, C. F. Schreck, C. S. O'Hern, H. Cao, E. M. Furst, E. R. Dufresne, *ACS Nano* **2011**, *5*, 6695–6700; b) S. H. Lee, C. M. Liddell, *Small* **2009**, *5*, 1957–1962; c) C. M. Liddell, C. J. Summers, *J. Colloid Interface Sci.* **2004**, *274*, 103–106; d) I. D. Hosein, S. H. Lee, C. M. Liddell, *Adv. Funct. Mater.* **2010**, *20*, 3085–3091; e) T. Ding, K. Song, K. Clays, C. H. Tung, *Adv. Mater.* **2009**, *21*, 1936–1940; f) Y. D. Hu, J. Y. Wang, C. N. Li, Q. Wang, H. Wang, J. T. Zhu, Y. J. Yang, *Langmuir* **2013**, *29*, 15529–15534; g) Y. D. Hu, J. Y. Wang, H. Wang, Q. Wang, J. T. Zhu, Y. J. Yang, *Langmuir* **2012**, *28*, 17186–17192.
- [4] a) J. Ge, Y. Hu, Y. Yin, *Angew. Chem. Int. Ed.* **2007**, *46*, 7428–7431; *Angew. Chem.* **2007**, *119*, 7572–7575; b) C. Gao, Z. Lu, Y. Liu, Q. Zhang, M. Chi, Q. Cheng, Y. Yin, *Angew. Chem. Int. Ed.* **2012**, *51*, 5629–5633; *Angew. Chem.* **2012**, *124*, 5727–5731; c) Y. Lu, Y. Yin, Z. Li, Y. Xia, *Langmuir* **2002**, *18*, 7722–7727; d) X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, S. A. Asher, *Adv. Mater.* **2001**, *13*, 1681–1684; e) X. L. Xu, S. A. Majetich, S. A. Asher, *J. Am. Chem. Soc.* **2002**, *124*, 13864–13868; f) T. S. Shim, S. H. Kim, J. Y. Sim, J. M. Lim, S. M. Yang, *Adv. Mater.* **2010**, *22*, 4494–4498.
- [5] a) L. He, Y. Hu, X. Han, Y. Lu, Z. Lu, Y. Yin, *Langmuir* **2011**, *27*, 13444–13450; b) Y. Hu, L. He, Y. Yin, *Small* **2012**, *8*, 3795–3799.
- [6] a) Y. Piao, J. Kim, H. Bin Na, D. Kim, J. S. Baek, M. K. Ko, J. H. Lee, M. Shokouhimehr, T. Hyeon, *Nat. Mater.* **2008**, *7*, 242–247; b) M. Wang, C. Gao, L. He, Q. Lu, J. Zhang, C. Tang, S. Zorba, Y. Yin, *J. Am. Chem. Soc.* **2013**, *135*, 15302–15305.
- [7] F. Xi'an, G. Jianguo, W. Wei, T. Guoxiu, *J. Phys. D* **2009**, *42*, 075006.
- [8] Y. Xia, B. Gates, Y. Yin, Y. Lu, *Adv. Mater.* **2000**, *12*, 693–713.
- [9] G. M. Whitesides, M. Boncheva, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4769–4774.
- [10] Y. Lu, Y. Yin, Y. Xia, *Adv. Mater.* **2001**, *13*, 415–420.
- [11] a) L. He, M. Wang, J. Ge, Y. Yin, *Acc. Chem. Res.* **2012**, *45*, 1431–1440; b) W. Luo, H. Ma, F. Mou, M. Zhu, J. Yan, J. Guan, *Adv. Mater.* **2014**, *26*, 1058–1064.
- [12] a) D. Frenkel, *Nat. Mater.* **2015**, *14*, 9–12; b) M. P. Taylor, J. Herzfeld, *Phys. Rev. A* **1991**, *43*, 1892–1905; c) K. T. Nguyen, F. Sciortino, C. De Michele, *Langmuir* **2014**, *30*, 4814–4819; d) M. Wang, L. He, S. Zorba, Y. Yin, *Nano Lett.* **2014**, *14*, 3966–3971; e) A. A. Shah, M. Ganesan, J. Jocz, M. J. Solomon, *ACS Nano* **2014**, *8*, 8095–8103; f) A. A. Shah, H. Kang, K. L. Kohlstedt, K. H. Ahn, S. C. Glotzer, C. W. Monroe, M. J. Solomon, *Small* **2012**, *8*, 1551–1562.
- [13] a) A. P. Hynninen, M. Dijkstra, *Phys. Rev. Lett.* **2005**, *94*, 138303; b) B. Evans, *Mol. Phys.* **2002**, *100*, 199–200; c) D. Frenkel, B. M. Mulder, *Mol. Phys.* **2002**, *100*, 201–217.
- [14] M. J. Solomon, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 158–167.

Received: February 24, 2015

Published online: April 29, 2015