

similar to that of a set of 14 independent molecules in a solution. Conversely, a semi-rigid, optimized acentric organization results in coherent second harmonic emission at the supramolecular level, the corresponding intensity from the dendrimer solution being almost proportional to  $N_{\text{monomer}}^2 \langle \beta_{\text{monomer}}^2 \rangle$ . The  $N_{\text{monomer}}^2$  dependence assumes a linear additive model, whereby the individual sub-units follow an interaction-free oriented gas behavior.

We have, therefore, clear evidence of quasi-optimized octupolar ordering in a dendrimer made of highly nonlinear ruthenium complexes. This is, to the best of our knowledge, the most efficient type of self-assembled supramolecular octupolar order reported to date. The availability of nonlinear octupolar dendrimers creates attractive possibilities for nanoscale photonic applications with other photonic functionalities, such as pertain to luminescence.

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## Superparamagnetic Photonic Crystals\*\*

By Xiangling Xu, Gary Friedman, Keith D. Humfeld, Sara A. Majetich, and Sanford A. Asher\*

There is intense scientific and technological interest in fabricating three-dimensional (3D) photonic bandgap materials.<sup>[1–5]</sup> Monodisperse highly charged colloidal particles readily self-assemble to form crystalline colloidal arrays (CCAs) in low ionic strength aqueous solutions.<sup>[6–13]</sup> They are the simplest photonic crystals showing bandgaps only in particular directions.<sup>[1,2,9–16]</sup> Though, these CCAs cannot show 3D photonic bandgaps, it may be possible to fabricate 3D photonic bandgap materials from face-centered cubic (fcc) particle arrays by utilizing oriented anisotropic spheres,<sup>[17–19]</sup> or by perturbing the array symmetry.<sup>[2]</sup> Here we show the fabrication of superparamagnetic photonic crystals from highly charged, monodisperse superparamagnetic ~134 nm polystyrene–iron oxide composite colloidal spheres. The lattice spacing of these superparamagnetic CCAs can be altered by magnetic fields. Soft solid polymerized CCAs (PCCAs) are synthesized by polymerizing the fcc array of superparamagnetic particles within a hydrogel matrix. Magnetic fields may be utilized to reversibly deform the PCCA lattice in one direction, which decreases the lattice symmetry and shifts the diffraction. This breaking of the fcc symmetry may be useful for creating unique photonic bandgap materials.

We modified the procedure of Yanase et al.<sup>[20]</sup> to produce superparamagnetic, highly charged, monodisperse colloidal particles. These particles were synthesized by emulsion polymerization of styrene, in the presence of ~10 nm iron oxide particles. The superparamagnetic nanoscale iron oxide particles were produced by the coprecipitation of ferric and ferrous chloride in ammonium hydroxide solution.<sup>[21,22]</sup> Before emulsion polymerization, the surface of these iron oxide particles was modified by adsorption of oleic acid.<sup>[23]</sup> Further details are given in the experimental section. After emulsion polymerization, the polystyrene particles containing iron oxide inclusions were harvested with a magnet. Transmission electron microscopy (TEM) measurements indicate a 134 nm number average diameter (polydispersity 7.5 %, Fig. 1). As expected, the polystyrene–iron oxide composite particles are superparamagnetic, and show no coercivity or remanence at room temperature.

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[\*] Prof. S. A. Asher, Dr. X. Xu  
Department of Chemistry, University of Pittsburgh  
Pittsburgh, PA 15260 (USA)  
E-mail: asher@pitt.edu

Prof. G. Friedman  
Electrical Engineering and Computer Science Department  
University of Illinois  
Chicago, IL 60607 (USA)

Dr. K. D. Humfeld, Prof. S. A. Majetich  
Department of Physics, Carnegie Mellon University  
Pittsburgh, PA 15213 (USA)

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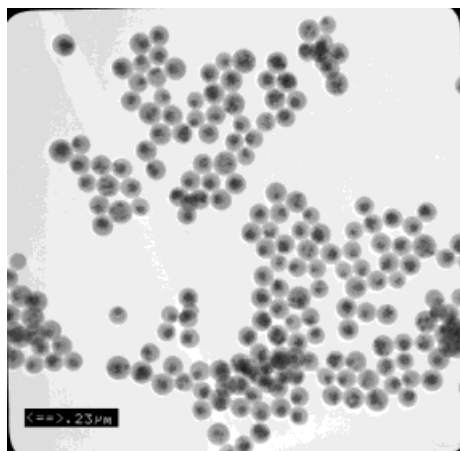


Fig. 1. TEM image of monodisperse polystyrene particles containing superparamagnetic nanoparticles. The aggregates of iron oxide nanoparticles appear as black dots in the larger polystyrene spheres. The polystyrene particle average diameter is 134 nm, with a polydispersity of 7.5 %.

These monodisperse superparamagnetic particles self-assemble into CCAs in deionized water, due to electrostatic repulsive interactions between the individual spherical particles. When an inhomogeneous magnetic field is applied to the CCA, an additional force occurs which causes the superparamagnetic particles to be attracted to the maximum of the local magnetic field gradient. Thus, the CCA is compressed along the magnetic field gradient. As shown in Figure 2, the diffraction wavelength blue-shifts as the magnetic field and its gradient increases. The lattice constant observed is determined by the balance between the magnetic packing forces and the spherically symmetric interparticle electrostatic repulsive forces. Therefore, the lattice constant is a minimum at the locus of the magnetic field gradient maximum and increases as the gradient decreases.

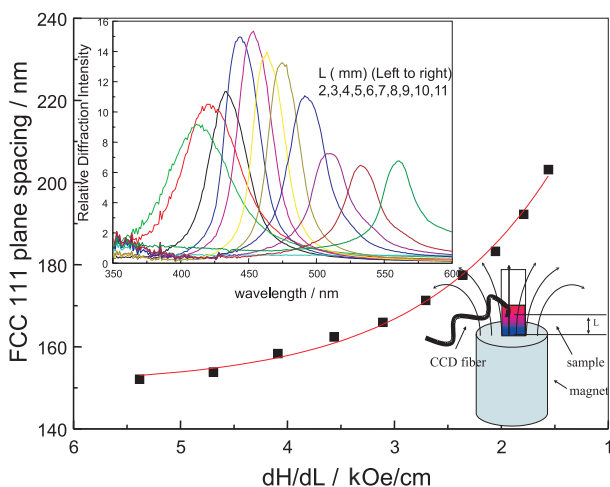


Fig. 2. Influence of the average magnetic field gradient,  $dH/dL$  on the lattice constant of a thick CCA composed of 134 nm superparamagnetic particles in deionized water (4.2 vol.-%). Top inset shows the dependence of the diffraction peak wavelength on the distance from the magnet. The lower right inset is an experimental schematic showing the CCA on top of a permanent magnet, with an optical fiber probe connected to a charge coupled device (CCD) spectrometer to determine the diffraction spectrum. The spatial dependence of the magnetic field was measured using a Hall probe.

Normally, CCAs do not self-assemble into highly ordered CCAs in high ionic strength aqueous solutions or in polar organic solvents due to the weak interparticle electrostatic interactions.<sup>[24,25]</sup> However, for superparamagnetic colloidal particles dispersed in these media, the magnetic field gradient exerts a force on these particles that induces a slow phase separation of these superparamagnetic particles into a high volume fraction phase near the wall of the sample holder. Then, these particles slowly pack into highly ordered CCAs there. Although a similar high volume fraction of these charged colloidal particles shows some ordering, highly ordered CCAs do not form since the high particle volume fraction is too viscous for the CCAs to anneal into a well ordered fcc structure. This magnetic self-assembly mechanism is probably similar to the mechanisms responsible for formation of close packed CCAs ordering during gravitational settling and the mechanism responsible for formation of close packed CCA ordering during fluid flow assembly,<sup>[26]</sup> where the fcc (111) crystal planes grow out from the surface as the next layer of particles pack against the previously stacked layer. Figure 3 shows the dependence of the diffraction wave-

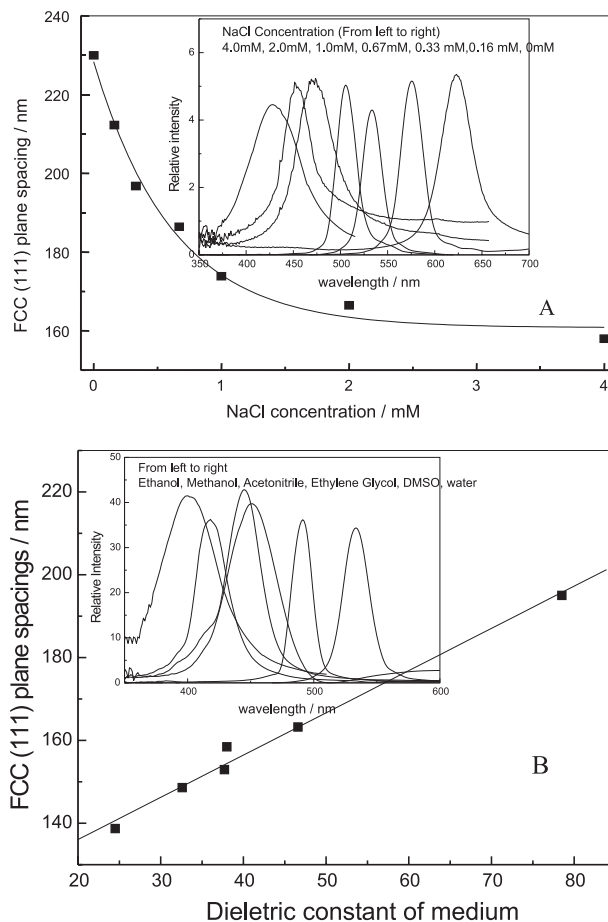


Fig. 3. Magnetic field induced packing of superparamagnetic particles in different media in a 4.6 kOe magnetic field with a 6.2 kOe/cm gradient. A) Magnetic assembly from a 5 % particle volume fraction NaCl aqueous solution. B) Magnetic self-assembly from 10 % particle volume fraction dispersions in ethanol (24.5), methanol (32.6), acetonitrile (37.7), ethylene glycol (38), dimethyl sulfoxide (DMSO) (46.6), and water (78). The dielectric constant of each solvent is given in parentheses.

length and the fcc (111) plane spacing on the NaCl concentration of aqueous CCAs and on the dielectric constant of a series of polar organic solvent CCAs. The fcc (111) plane spacing decreases as the NaCl concentration increases, and as the organic solvent dielectric constant increases.

We can form anisotropic arrays by embedding the superparamagnetic CCA in soft hydrogels and then perturbing the crystal structure with a magnetic field. We dispersed the superparamagnetic particles in an aqueous solution containing acrylamide and bisacrylamide. After the fcc CCA self-assembled, we thermally polymerized it into a hydrogel (PCCA).<sup>[27,28]</sup> As shown in Figure 4, the superparamagnetic PCCA film fixed on one-end quickly blue shifts from 787 nm to 783 nm upon imposition of a magnetic field next to the free end. Over an additional 60 min the diffraction further blue shifts to an equilibrium value of ~777 nm. This slower process is presumably associated with the creep of this viscoelastic hydrogel. The resulting anisotropic strain applied by magnetic field on the PCCA film, elongates the lattice constant along the field direction. Therefore the lattice constant decreases along directions normal to the strain direction, due to conservation of volume. As also shown in Figure 4, the magnetic field induced deformation of the superparamagnetic PCCA is fully reversible. The magnetic field can, thus, be used to both tune the diffraction wavelength and to alter the crystal structure.

In conclusion, these monodisperse, highly charged, superparamagnetic colloidal particles enable fabrication of magnetically controlled photonic crystals. In addition, this superparamagnetic particle magnetic self-assembly fabricates photonic crystals in media that were previously incompatible with CCA formation. This self-assembly in non-aqueous systems enables utilization of non-aqueous chemical processing to develop novel photonic crystal materials and applications.

Magnetic fields can be used to both alter the diffraction wavelength and to control the crystal structure and lattice plane spacing. The magnetic field induced perturbation of the PCCA fcc symmetry alters the diffraction properties of these materials and creates unique photonic crystal materials.

### Experimental

Nanoscale iron oxide was prepared by the coprecipitation of ferric and ferrous ions in ammonium hydroxide solution. 10.8 g of FeCl<sub>3</sub>·6H<sub>2</sub>O (J. T. Baker), and 4.0 g FeCl<sub>2</sub>·4H<sub>2</sub>O (Sigma) was dissolved in 50 mL of water. The resulting solution was poured with vigorous stirring into 500 mL of a 1.0 M NH<sub>3</sub>·H<sub>2</sub>O solution. The black precipitate was collected with a magnet. 500 mL of 1 M

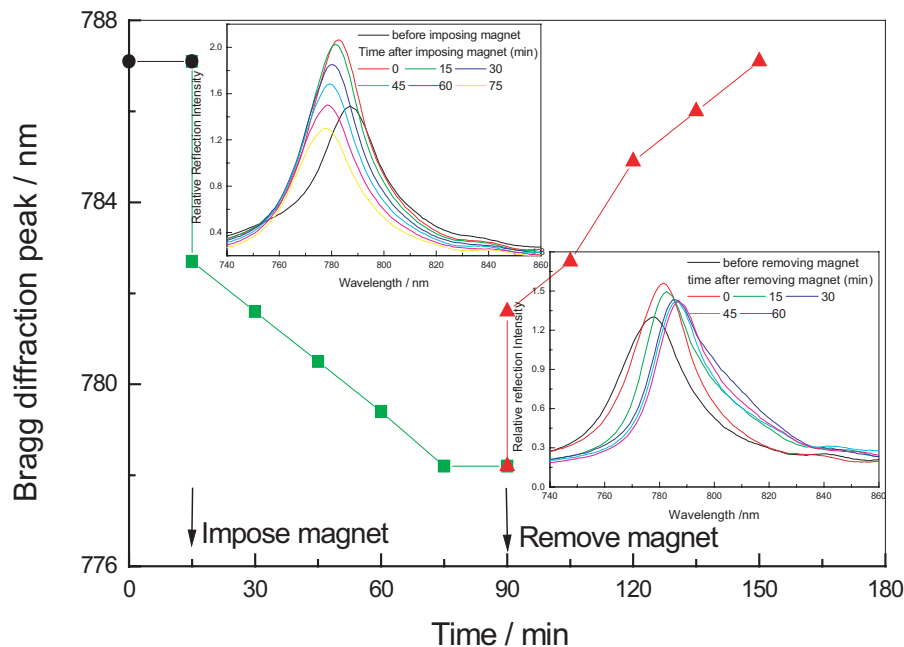


Fig. 4. Response of superparamagnetic PCCA film to a 2.4 kOe magnetic field with a 3.2 kOe/cm gradient. After imposition of the magnetic field the Bragg diffraction blueshifted from 787 nm to 777 nm. This shift was fully reversible; the diffraction redshifted back to 787 nm after removing the magnetic field.

TMAOH (tetramethylammonium hydroxide, Aldrich) solution was added to the precipitate and the mixture was sonicated for 1 h. Our particles show X-ray diffraction spacing close to those of both magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>), which are inverse spinel structures. The relative diffraction intensities indicate that they are closer to maghemite than magnetite. TEM measurements show a broad size distribution (2–15 nm), with an average diameter ~10 nm. At room temperature neither coercivity nor remanence was observed, indicating that nanoparticles are superparamagnetic.

Superparamagnetic, monodisperse and charged polystyrene spheres were synthesized by emulsion polymerization in presence of iron oxide nanoparticles. A jacketed cylindrical reaction vessel was charged with 180 mL of water and 20 mL of the iron oxide dispersion. After 30 min of deoxygenating, 30 mL styrene (St, Aldrich), 3.0 mL methyl methacrylate (MMA, Aldrich), and 0.2 g sodium styrene sulfonate (NaSS, Polyscience) were added into the vessel. The temperature was increased to 70 °C and 2.0 g ammonium persulfate (APS, Aldrich) was added to initiate polymerization, which reacted for 5 h. The polystyrene particles containing iron oxide were harvested by a magnet. TEM measurements indicate that these particles are monodisperse with a ~134 nm diameter. Conductometric titrations show a surface charge of 6.3 μC/cm<sup>2</sup>. Flame atomic absorption and magnetic measurements obtained by using a superconducting quantum interference device (SQUID) magnetometer both indicate a 17.1 wt.-% iron oxide content. As expected, the dry magnetic polystyrene particle powder shows no coercivity or remanence.

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## Core–Shell Structures Formed by the Solvent-Controlled Precipitation of Luminescent CdTe Nanocrystals on Latex Spheres\*\*

By Igor L. Radtchenko, Gleb B. Sukhorukov, Nikolai Gaponik, Andreas Kornowski, Andrey L. Rogach,\* and Helmuth Möhwald

A novel method of fabricating core–shell structures, comprising monodisperse submicrometer-sized latex spheres as cores and nanocrystals as shells, is demonstrated. The coating was formed by a solvent-controlled precipitation of CdTe nanocrystals from aqueous solutions either by adding ethanol or by changing the pH. The proper choice of the concentration of the latex particles and nanocrystals provided a homogeneous and complete coverage of colloidal cores with luminescent shells of desirable thickness in the range of 15–40 nm as confirmed by transmission electron microscopy (TEM) and confocal fluorescence microscopy.

Engineering of colloidal surfaces is a current topic of applied chemistry in the field of developing new materials with

tailored properties. Research on composite colloidal particles (core–shell structures) has received sufficient interest due to various applications expected in the areas of coatings, electronics, photonics, and catalysis.<sup>[1]</sup> Formation of shells on colloidal particles yields composites possessing properties significantly different from that of the core, e.g., increased stability, adhesion, surface area, magnetic and optical properties. There are several approaches to fabricate shells on colloidal cores, which involve, for instance, surface chemical reactions,<sup>[2]</sup> precipitation of inorganic salts<sup>[3,4]</sup> or colloidal particles,<sup>[5]</sup> and the layer-by-layer (LbL) assembly of charged macromolecules or nanoparticles.<sup>[6–9]</sup> All these methods have their own advantages and drawbacks for the preparation of coated particles, resulting in different uniformity, thickness, and composition of the shells.

Colloidally synthesized semiconductor nanocrystals with tailored surface properties (through the proper choice of stabilizing molecules) and sufficiently strong luminescence tunable through the particle size<sup>[10]</sup> can successfully be used for the fabrication of luminescent shells on colloidal particles. It was shown<sup>[11,12]</sup> that a shell structure comprising polyelectrolyte multilayers and luminescent CdTe nanocrystals<sup>[13]</sup> can be deposited on latex particles using the step-wise approach of LbL alternate adsorption. This method of the nanocomposite assembly provides a defined shell composition on the colloidal core with a shell thickness being a function of the number of deposited layers. The LbL approach can be applied to coat charged colloidal particles of different shapes with sizes ranging from 0.1 to 10  $\mu\text{m}$ .<sup>[6–9]</sup> However, the procedure is sufficiently time consuming because it requires the removal of non-bound polyelectrolytes and nanocrystals at each step of the assembly. The presence of the polymer component in the nanocrystal-containing shells is also not always desirable. The nanoparticles must carry sufficient charge to be used in the LbL assembly technique.

We have developed and report in this paper a new method of coating colloidal particles through the controlled precipitation of CdTe nanocrystals by means of their aggregation in solution on latex spheres. The approach demonstrated is a variation of heteroaggregation phenomena in colloidal environments. The aggregation of nanocrystals on colloidal cores was induced, for the first time, by the solvent–non-solvent-pair precipitation technique, which was previously successfully used to separate semiconductor nanocrystals by size.<sup>[14,15]</sup> Colloidal cores statistically harvest aggregated nanocrystals (Scheme 1). Alternatively, precipitation of nanocrystals can be driven by changing their solubility through the change of pH of the aqueous solution.<sup>[5]</sup> The technique described herein allows the production of uniform complete shells in one step on a time scale of minutes, which is a drastic acceleration in comparison to the multi-step LbL approach that needs hours or even days to complete. The thickness of the shells can be effectively controlled through the proper choice of the concentration ratio of colloidal particles serving as cores and the precipitated species. As considered theoretically,<sup>[16]</sup> there are certain concentration windows for colloidal cores and the

[\*] Dr. A. L. Rogach,<sup>[+]</sup> Dr. N. Gaponik,<sup>[+]</sup> A. Kornowski  
 Institute of Physical Chemistry, University of Hamburg  
 D-20146 Hamburg (Germany)  
 E-mail: rogach@chemie.uni-hamburg.de

I. L. Radtchenko, Dr. G. B. Sukhorukov, Prof. H. Möhwald  
 Max Planck Institute of Colloids and Interfaces  
 D-14424 Potsdam (Germany)

[+] On leave from: Physico-Chemical Research Institute, Belarusian State University, Minsk, Belarus.

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