

# Magnetic Assembly of Nonmagnetic Particles into Photonic Structures

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## Experimental Section

**Materials.** Diethylene glycol (DEG, reagent grade), ethanol (denatured), and sodium hydroxide (NaOH, 98.8%) were purchased from Fisher Scientific. Anhydrous iron(III) chloride (FeCl<sub>3</sub>, 98%) was purchased from Riedel-de Haën. Poly(acrylic acid) (PAA, MW = 1800) Styrene (Reagent Plus grade), Methyl Methacrylate (99%) and ammonium persulfate (A. C. S. reagent grade) were obtained from Sigma-Aldrich. P-styrene sulfonic acid sodium salt was supplied by TCI America. All chemicals were directly used as received without further treatment.

**Synthesis of Superparamagnetic Fe<sub>3</sub>O<sub>4</sub> CNCs.** Highly water-soluble magnetite nanocrystals with average size of 11.5 nm were synthesized in solution at high temperature.<sup>1</sup> In a typical synthesis, a mixture of 4 mmol of PAA, 2 mmol of FeCl<sub>3</sub>, and 15 mL of DEG was heated to 220 °C in a nitrogen atmosphere with vigorous stirring. 4 mL of NaOH/DEG stock solution (2.5 mol/L) was then injected into the above solution which turned black immediately. After the temperature reached 220 °C again, another 5 mL of FeCl<sub>3</sub> stock solution (0.4 mol/L) was added into the reaction mixture. The temperature dropped to around 200 °C. Another 3 mL of NaOH/DEG stock solution (2.5 mol/L) was then injected at 220 °C. The resulting mixture was further heated for 10 min to yield 11.5 nm Fe<sub>3</sub>O<sub>4</sub> nanocrystals. These colloids were first washed with a mixture of deionized (DI) water and ethanol several times to remove additional surfactant and salt, and finally dispersed in 1 mL of DI water. The volume fraction of Fe<sub>3</sub>O<sub>4</sub> in the final ferrofluid was about 5%.

**Synthesis of Polystyrene spheres.** Monodisperse Polystyrene spheres with size of 185 nm were synthesized through an emulsion polymerization method.<sup>2</sup> 50 mL of deionized water was degassed with Nitrogen for 30 min. 3.3 mL of styrene and 0.5 mL of methyl methacrylate were injected into the above DI water. 0.05 g p-styrene sulfonic acid sodium salt in 1 mL DI water was then added. The mixture solution was

further degassed with Nitrogen for 30 min and then heated to 70 °C. 0.5 g ammonium persulfate in 1 mL DI water was injected to initiate the polymerization. The reaction mixture was kept stirring at 70 °C for 7 h before cooled down to room temperature. The as-obtained polymer spheres were washed with DI water several times and dispersed in DI water. The volume fraction of polymer spheres was about 15%.

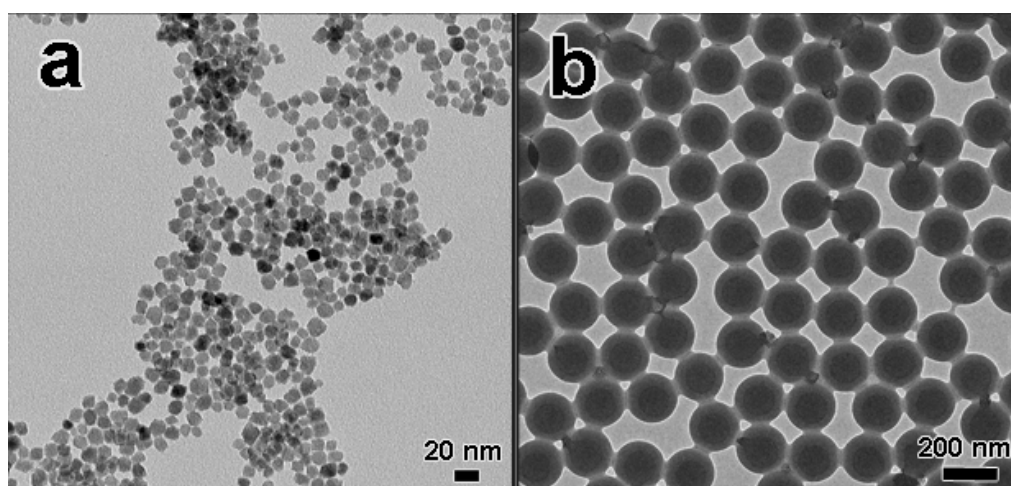
**Characterization of Fe<sub>3</sub>O<sub>4</sub> CNCs and polystyrene spheres.** The morphology and size distribution of the Fe<sub>3</sub>O<sub>4</sub> CNCs and polystyrene spheres were characterized under a Tecnai T12 transmission electron microscope (TEM). Colloids dispersed in water at an appropriate concentration were cast onto a carbon-coated copper grid, followed by evaporation under vacuum at room temperature.

### **Numerical calculation of the local concentration of nonmagnetic PS beads in ferrofluid**

To monitor the local concentration distribution of nonmagnetic beads in ferrofluid under external magnetic field, a mass transport model was developed to solve convection-diffusion equations with given boundary condition. We consider a mixture of PS beads and ferrofluid in a confined film, and the ferrofluid is assumed to be a continuum relative to the larger nonmagnetic beads. When an external magnetic field is applied to the mixture, magnetic packing force,  $F_m = -\mu_0 V_{PS} M_f \nabla H$ , is exerted to

the nonmagnetic beads, where  $\mu_0$  is the permeability of free space,  $V_{PS}$  is the volume of the non-magnetic bead,  $M_f$  is the magnetization of the ferrofluid, and  $H$  is the magnetic field. Thus, nonmagnetic beads move towards the region of the lowest magnetic field gradient with terminal velocity,  $v = -\frac{2R_p^2 \mu_0 M_f \nabla H}{9\eta}$  where

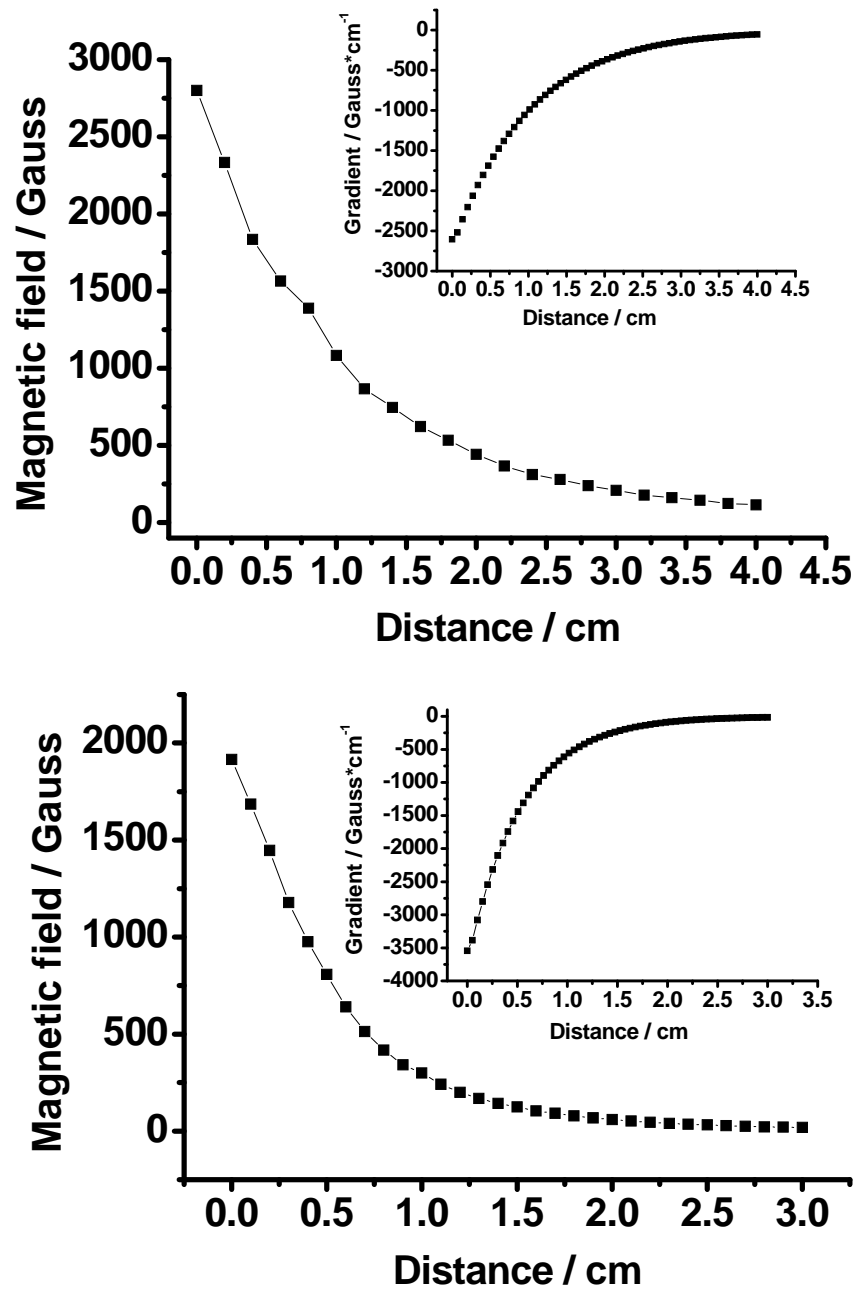
$R_p$  is the radius of nonmagnetic bead, and  $\eta$  is the viscosity of the medium. We assumed that the relaxation time is short compared to the time span of interest. Total nonmagnetic bead flux can be stated as  $J_{PS} = -D\nabla C + vC$  including magnetically induced drift flux and diffusion flux, where  $D$  is a diffusion constant, and  $C$  is the concentration of PS beads. Finally, local concentration of nonmagnetic beads can be evaluated by incorporating total flux into continuity equation,  $\frac{\partial C}{\partial t} + \nabla \cdot J_{PS} = 0$ , and 1 dimensional calculation was performed to solve this equation. In order to consider a close packing of nonmagnetic beads, we used a diffusion constant adjusted with the compressibility factor that diverges as local concentration approaches to close packing, which keeps the local concentration close to close packing. Detail discussion of adjusted diffusion constant can be found elsewhere<sup>3,4</sup>.



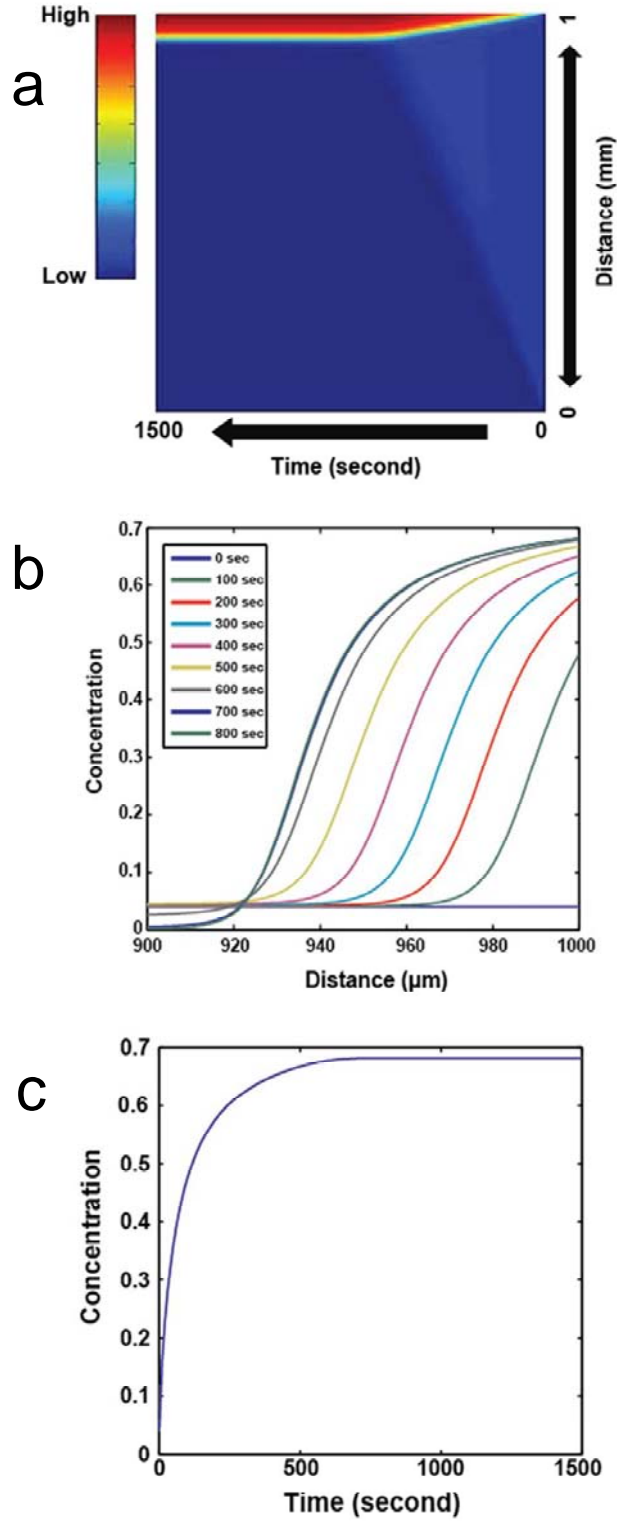
**Figure S1.** TEM images of (a) 11.5-nm  $\text{Fe}_3\text{O}_4$  nanocrystals and (b) 185-nm polystyrene spheres

Table S1. The strength and gradient of the magnetic field in Figure 3.

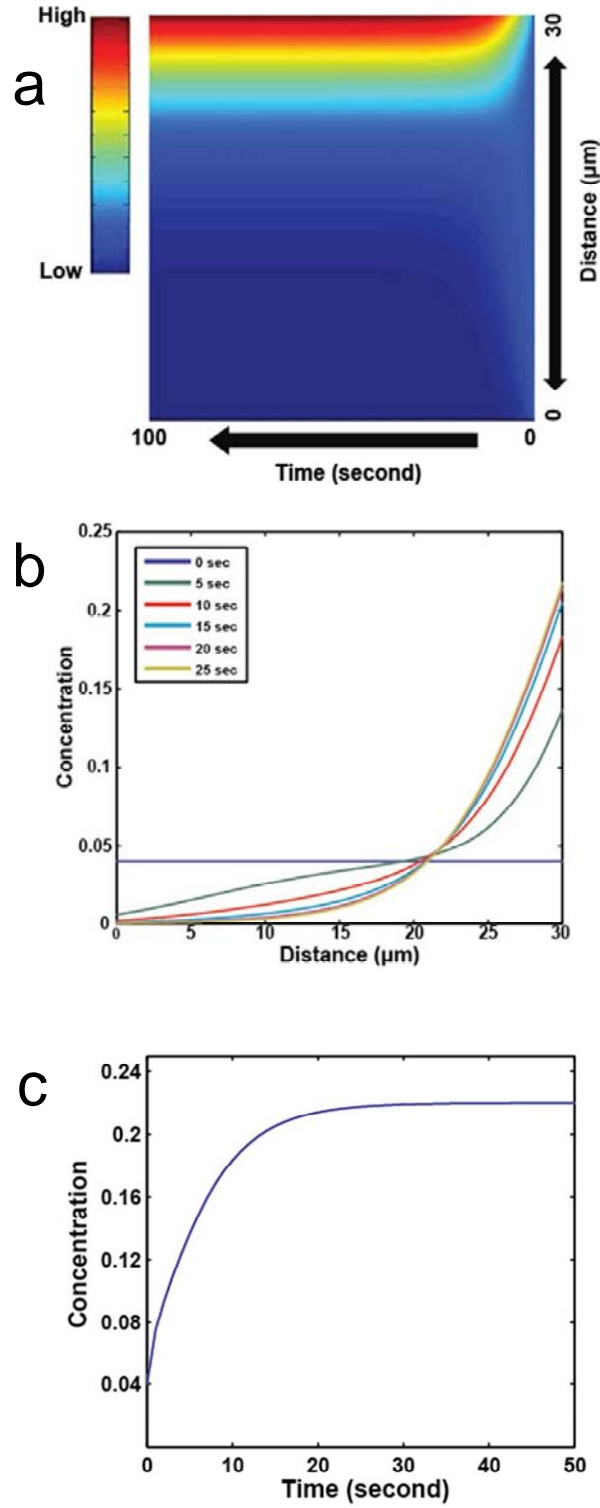
Distance (cm)	H (G)	Gradient (G/cm)
3.0	210	150
2.7	260	180
2.4	311	220
2.1	404	375
1.8	534	450
1.5	684	570
1.2	866	842



**Figure S2.** Spatial distribution of the magnetic field strength and gradient (inset) measured using a Hall probe for the NdFeB magnets used in the experiments. (Top) 1 inch cubic magnet used in spectrum measurement; (Bottom) 0.1×0.5×0.5 inch disk magnet used in optical observation.



**Figure S3.** Local concentration of nonmagnetic beads in ferrofluid in a 1-mm thick liquid film under an external magnetic field. (a) Local concentration profile at time and location of interest. (b) Local concentration in 100  $\mu\text{m}$  from the top region of the film. (c) Local concentration evolution at the top region of the film.



**Figure S4.** Local concentration of the mixture of nonmagnetic beads and ferrofluid in a 30- $\mu\text{m}$  thick film under an external magnetic field. (a) Local concentration profile at time and location of interest. (b) Local concentration in entire 30  $\mu\text{m}$  cell. (c) Local concentration evolution at the top region of the film.

## Reference

1. Ge, J. P.; Hu, Y. X.; Biasini, M.; Dong, C. L.; Guo, J. H.; Beyermann, W. P.; Yin, Y. D. *Chemistry-a European Journal* **2007**, *13*, (25), 7153-7161.
2. Qiu, D.; Cosgrove, T.; Howe, A. M. *Macromolecular Chemistry and Physics* **2005**, *206*, 2233-2238.
3. A. F. Routh, W. B. Zimmerman, *Chemical Engineering Science* **2004**, *59*, 2961-2968
4. S. G. Yiantsios, B. G. Higgins, *Physics of Fluids* **2006**, *18*, 082103