

Functional Magnetic Nanoparticle Assemblies: Formation, Collective Behavior, and Future Directions

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Self-assembly involves the spontaneous formation of complex structures from simpler objects due to their interaction forces. In biology, self-assembly is more commonly referred to as molecular recognition, while in metallurgy, it leads to crystallization of atoms into solids. On the microscale, polymer beads can form colloidal crystals,^{1–3} and macromolecules such as tobacco mosaic virus can form liquid crystals. On the nanoscale, small particles can pack into ordered lattices.^{4–7} Figure 1 shows an image of a three-dimensional ordered lattice or nanoparticle crystal formed from manganese oxide nanoparticles. Block copolymers can also form self-organized structures when like blocks phase segregate.⁸ In this Perspective, we discuss recent developments in nanoparticle self-assembly, the collective behavior of the self-assembled structures of magnetic nanoparticles, and the future challenges in this field.

There are several similarities in self-assembly on different length scales. The monodispersity of the atomic, molecular, or particle building blocks enables them to form highly ordered structures. These building blocks can move easily and have time to sample different configurations in order to minimize their free energy. It is unsurprising that self-assembly so often occurs in a liquid medium.

There are also significant differences that depend on the length scale of the self-organizing entities. On the micrometer scale, most self-assembly studies have used aqueous dispersions of spherical polymer or silica beads that are charge-stabilized. Provided that the surface groups (e.g., sulfonates) are evenly distributed over the particle surface, and the electric field generated by a particle is isotropic. The balance between electrostatic repulsion and van der Waals attraction leads the particles to form ordered arrays.

ABSTRACT This Perspective describes recent progress in the development of functional magnetic nanoparticle assemblies. After describing the formation of two- and three-dimensional particle arrays in terms of the size-dependent driving forces, we focus on magnetic nanoparticle arrays. We discuss how the self-organized structure can modify the magnetic behavior, relative to that of isolated particles. We highlight an important development, described in this issue of *ACS Nano* by Kostianin and co-workers, who have demonstrated not only the novel aqueous self-assembly of magnetic particles but also controlled and reversible disassembly. Finally, we explore two inter-related future directions for self-assembly of magnetic nanoparticles: the formation of more complex, hierarchical structures and the integration of self-assembly with fabrication techniques for electronic devices.

Two-dimensional structures are frequently used after drying to form close-packed arrangements. Three-dimensional arrays can be dried or dispersed in liquids as colloidal crystals. In colloidal crystals, the edge-to-edge separation between particles can be tuned homogeneously by adjusting the salt concentration to change the electrostatic repulsion force. It can be shifted inhomogeneously by applying a magnetic field gradient if the colloidal particles are magnetic.⁹

On the nanometer scale, most self-assembly studies have used surfactant-coated particles dispersed in organic solvents. The primary forces leading to self-assembly are isotropic steric repulsion due to the surfactant coatings, plus van der Waals attraction of the particle cores. Nothing fundamental precludes self-assembly of aqueous dispersions of nanoparticles, but it is much more challenging to control the surface charge uniformity. Without this, collisions between particles lead to irreversible agglomeration and the formation of poorly ordered structures.

To create ordered three-dimensional arrays of surfactant-coated nanoparticles in organic solvents, the dispersion is destabilized through the slow diffusion of a poorly coordinating solvent.¹⁰ Figure 2 shows a comparison of the small-angle X-ray scattering

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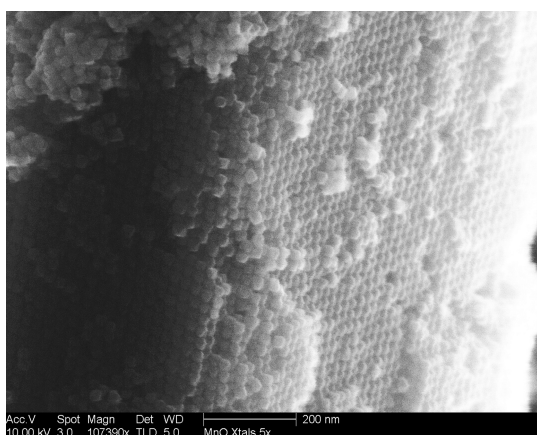


Figure 1. Crystal formed from faceted MnO core/Mn₃O₄ shell nanoparticles.

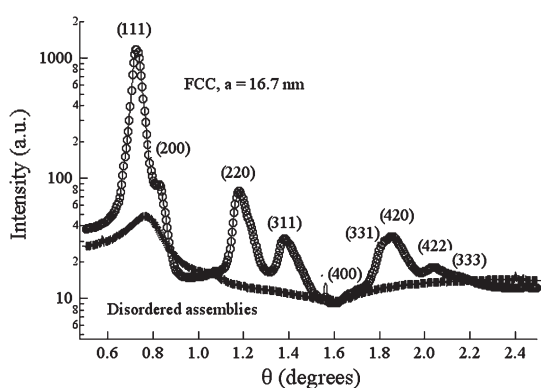


Figure 2. Small-angle X-ray scattering patterns of nanoparticle crystals showing a face-centered cubic structure assemblies prepared from surfactant-coated 8.5 nm Fe nanoparticles. Rapid solvent evaporation generates a disordered assembly, while slow growth leads to fcc packing into nanoparticle crystals. Reproduced with permission from ref 11. Copyright 2005 Institute of Physics.

intensity for a nanoparticle crystal and for a nanoparticle assembly prepared by direct evaporation of a toluene dispersion of the same particles.¹¹ At room temperature, the drying process occurs over tens of minutes and the particles are frozen in with a glassy structural order. Nanoparticle crystals are formed over a period of weeks at room temperature or over a period of hours when the dispersion is heated, as with the nanoparticle crystal shown in Figure 1. Structures formed from spherical particles tend to have face-centered cubic or hexagonal close-packed lattices, though body-centered cubic packing has been observed for small nanoparticles due to entropic considerations.^{4,12}

Two-dimensional arrays are readily formed by evaporation of a surfactant-coated particle dispersion

onto a solid substrate, but this leads to arrays of varying thickness. Once the drying front of the organic solvent has passed by, the particles are immobile, so these arrays tend to have more structural defects. High-quality, large-area monolayer arrays can be formed on liquid surfaces, where the particles are kept in the interfacial plane by surface tension but are mobile within the plane.^{7,13}

The development of high-temperature chemical syntheses of nanoparticles that self-assemble into ordered arrays has enabled more sophisticated studies of nanoparticle interactions. For example, gold nanoparticles have a surface plasmon resonance with a peak wavelength that is sensitive to the local dielectric environment.⁴ Since the dielectric properties of metals are very different from those of surfactants

and solvents, when gold nanoparticles are packed into assemblies, there is a pronounced shift in the plasmon peak. The shift is comparable for nanoparticle crystals and for glassy assemblies of plasmonic particles.

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In contrast, the collective magnetic behavior of nanoparticle assemblies is very sensitive to the structural order. Small nanoparticles made from ferro- or ferrimagnetic materials are single magnetic domains and act like tiny magnetic dipoles. The typical 2–4 nm separations between cores mean that interparticle coupling is almost purely magnetostatic. The field generated by one dipole can be either magnetizing or demagnetizing to another dipole, depending on its location. Moreover, the strength of the dipolar field decays as the inverse cube of the distance, giving rise to subtle long-range effects. Magnetically coupled regions on the order of the structural coherence length of ~ 150 nm were observed for 12 nm ϵ -Co nanoparticles,¹⁴ but domains as large as 55 μm have been observed in densely packed arrays of 8 nm ϵ -Co particles.¹⁵ With 13 nm Fe₃O₄ nanoparticles in dense, highly ordered arrays, the magnetic domains are stable almost up to the Curie temperature and then show an abrupt phase transition to a demagnetized state.¹⁶ This dipolar ferromagnetic state was predicted many years ago based on calculations for arrays of point dipoles.¹⁷ With

nanoparticle assemblies, this effect can be realized at and above room temperature. The frequency-dependent collective behavior of nanoparticles also shows large differences relative to that of isolated particles. An ensemble of ideal, non-interacting magnetic nanoparticles is said to be superparamagnetic above a blocking temperature since the particles equilibrate within the measurement time, and no magnetic hysteresis is observed. This can also be interpreted in terms of a blocking frequency for a fixed temperature, above which the spins appear to be frozen. When magnetic nanoparticles interact but are not in ordered assemblies, the inhomogeneity of the interactions leads to a broad range of relaxation frequencies.¹⁸ It remains to be seen whether ordered arrays in the dipolar ferromagnetic state will show collective frequency-dependent responses. If they do, such assemblies could be designed for high-frequency applications requiring high permeability but low eddy current losses.

In this issue of *ACS Nano*, Kostiainen *et al.* report both the controlled assembly and the reversible disassembly of nanostructures based on artificial ferritins.¹⁹ Artificial ferritins are a fascinating model system for self-assembly because they enable small nanoparticles to be prepared with both a steric coating and a polar surface, so that they form stable dispersions in water.²⁰ Crystallization is accomplished by the addition of salt to change the thickness of the electrostatic double layer surrounding the particles and shift the balance of interaction forces. In their assembled form, the structural order is relatively short-range, but even so, dipolar ferromagnetic behavior is observed up to 400 K for 8 nm $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ particles, with 4 nm edge-to-edge separation. The corresponding isolated particles are superparamagnetic. The ability to form and to disperse a nanoparticle crystal in water would be essential for any biological application using a nanoparticle assembly. A magnetic

nanoparticle assembly would be easier to guide within the body because the ratio of magnetic to viscous drag forces is higher than for isolated nanoparticles and because Brownian motion effects are reduced.²¹ While photostimulated dispersion may not be suitable for *in vitro* drug delivery applications, Kostiainen and co-workers have shown that techniques for controlled disassembly are also important.

OUTLOOK AND FUTURE CHALLENGES

Nanoscale self-assembly is a large field, and there are sure to be exciting developments in many different directions. In this Perspective, two of the important challenges are singled out: hierarchical self-assembly and the ability to integrate self-assembled structures with electronics.

Mother Nature is an expert in hierarchical self-assembly, which extends from the molecular to the cellular level and beyond to whole organisms and populations of species. In comparison, nanoscience is at a fairly rudimentary stage of hierarchical self-assembly. Binary lattices of nanoparticles with long-range order have been prepared.⁶ There have been efforts to guide the assembly of submicrometer particles with patterned templates.²² These approaches aim for highly ordered and mainly two-dimensional structures. Biomimetic materials synthesis targets more complex, three-dimensional structures such as artificial collagen²³ and bone.²⁴ The work of Kostiainen *et al.* shows that engineered biomimetic materials can be combined with nanoparticle self-assembly, taking advantage of the strengths of each.

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Hierarchical self-assembly will be needed to integrate self-assembled structures with electronics, but there are many other issues to address, as well. Breakthroughs such as the discovery of the quantum Hall effect and giant magnetoresistance required high-quality samples with crystallographic orientation and epitaxial interfaces. Electronic connections to single nanomagnets were essential for the demonstration of spin-polarized current-induced switching and current-induced microwave generation in a nanomagnet.²⁵ However, in self-assembled structures, there is little control over the crystallographic orientation. Self-organized arrays are formed from superparamagnetic particles; if the magnetic moments were blocked, chains would be formed instead. Therefore, arrays with a high degree of crystallographic orientation cannot be formed by self-assembly of spherical particles in a magnetic field. Faceted particles such as magnetic nanocubes are a possible solution to the orientation problem, provided they are single-grained.²⁶ A greater challenge is the attachment of electrical leads since, with an organic surfactant coating, both the nature of the electrical contact and the surface or interface quality could vary from particle to particle. Even if electrons tunnel onto and off of a nanoparticle, the non-uniformity of the tunnel barriers would be limiting for many applications. One possible solution is to use self-assembled nanoparticle monolayers as an etch mask for a multilayer thin film. Figure 3 shows an antidot array etch mask, though dot arrays have also been prepared.²⁷ Such nanomasks combine the small feature size, high density, and potential low costs of self-assembly processes and can be used with existing pattern transfer techniques such as reactive ion etching. Arrays of holes can be etched using an antidot etch mask and then back-filled, or the surfactant surrounding the nanoparticle monolayer can be removed to form a dot array

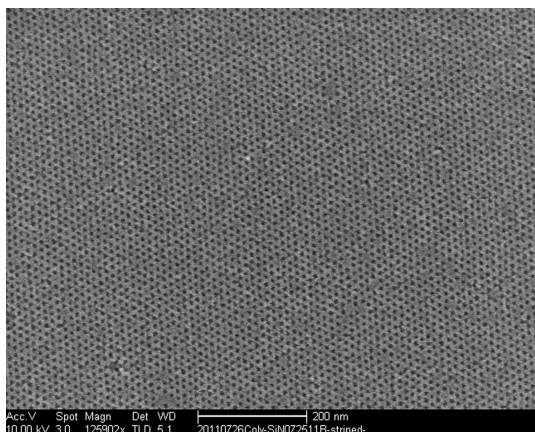


Figure 3. Scanning electron microscopy image of an antidot lattice prepared from surfactant-coated 12 nm iron oxide nanoparticles, following aluminum deposition and particle removal.

whose pattern is transferred into the underlying thin film by etching. Provided the thin film stack has conductive layers at the top and bottom, it is possible to make good electrical connections to the etched nanopillar array.

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REFERENCES AND NOTES

- Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. Mechanism of Formation of Two-Dimensional Crystals from Latex Particles on Substrates. *Langmuir* **1992**, *8*, 3183–3190.
- Hulteen, J. C.; Van Duyne, R. P. Nanosphere Lithography: A Materials General Fabrication Process for Periodic Particle Array Surfaces. *J. Vac. Sci. Technol., A* **1995**, *13*, 1553–1558.
- Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. Single-Crystal Colloidal Multilayers of Controlled Thickness. *Chem. Mater.* **1999**, *11*, 2132–2140.
- Whetten, R. L.; Shafiqullin, M. N.; Khoury, J. T.; Schaaff, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. Crystal Structure of Molecular Gold Nanocrystal Arrays. *Acc. Chem. Res.* **1999**, *32*, 397–406.
- Petit, C.; Russier, V.; Pileni, M. P. Effect of the Structure of Cobalt Nanocrystal Organization on the Collective Magnetic Properties. *J. Phys. Chem. B* **2003**, *107*, 10333–10336.
- Dong, A.; Ye, X.; Chen, J.; Murray, C. B. Two-Dimensional Binary and Ternary Nanocrystal Superlattices: The Case of Monolayers and Bilayers. *Nano Lett.* **2011**, *11*, 1804–1809.
- Bigioni, T. P.; Lin, X.-M.; Nguyen, T. T.; Corwin, E. I.; Witten, T. A.; Jaeger, H. M.

- Kinetically Driven Self Assembly of Highly Ordered Nanoparticle Monolayers. *Nat. Mater.* **2006**, *5*, 265–270.
- Park, S.; Lee, D. H.; Xu, J.; Kim, B.; Hong, S. W.; Jeong, U.; Xu, T.; Russell, T. P. Macroscopic 10-Terabit-per-Square-Inch Arrays from Block Copolymers with Lateral Order. *Science* **2009**, *323*, 1030–1033.
- Xu, X. L.; Majetich, S. A.; Asher, S. A. Mesoscopic Monodisperse Ferromagnetic Colloids Enable Magnetically Controlled Photonic Crystals. *J. Am. Chem. Soc.* **2002**, *124*, 13864–13868.
- Talpin, D. V.; Shevchenko, E. V.; Kornowski, A.; Gaponik, N.; Haase, M.; Rogach, A. L.; Weller, H. A New Approach To Crystallize CdSe Nanoparticles into Ordered Three Dimensional Structures. *Adv. Mater.* **2001**, *13*, 1868–1871.
- Farrell, D.; Cheng, Y.; Kan, S.; Sachan, M.; Ding, Y.; Majetich, S. A.; Yang, L. Iron Nanoparticle Assemblies: Structures and Magnetic Behavior. *J. Phys.: Conf. Ser.* **2005**, *17*, 185.
- Yamamoto, S.; Farrell, D.; Majetich, S. A. Direct Imaging of Self-Assembled Magnetic Nanoparticle Arrays: Phase Stability and Magnetic Effects on Morphology. *Phys. Rev. B* **2002**, *65*, 224431.
- Sachan, M.; Walrath, N. D.; Majetich, S. A.; Krycka, K.; Kao, C.-C. Interaction Effects within Langmuir Layers and Crystals of ϵ -Co Nanoparticles. *J. Appl. Phys.* **2006**, *99*, 08C302.
- Puntes, V. P.; Gorostiza, P.; Aruguete, D. M.; Bastus, N. G.; Alivisatos, A. P. Collective Behaviour in Two-Dimensional Cobalt Nanoparticle Assemblies Observed by Magnetic Force Microscopy. *Nat. Mater.* **2004**, *3*, 263–268.
- Yamamoto, K.; Majetich, S. A.; McCartney, M. R.; Sachan, M.; Yamamoto, S.; Hirayama, T. Direct Visualization of Dipolar Ferromagnetism and Domain Structures in Co Nanoparticle Monolayers. *Appl. Phys. Lett.* **2008**, *93*, 082502.
- Yamamoto, K.; Hogg, C. R.; Yamamoto, S.; Hirayama, T.; Majetich, S. A. Dipolar Ferromagnetic Phase Transition in Fe_3O_4 Nanoparticle Arrays. *Appl. Phys. Lett.* **2011**, *98*, 072509.
- Luttinger, J. M.; L. Tisza, L. Theory of Dipolar Interactions in Crystals. *Phys. Rev.* **1946**, *70*, 954–964.
- Jonsson, T.; Nordblad, P.; Svedlindh, P. Dynamic Study of Dipole–Dipole Interaction Effects in a Magnetic Nanoparticle System. *Phys. Rev. B* **1998**, *57*, 497–504.
- Kostiainen, M.; Pierpaolo, C.; Fornara, M.; Hiekkataipale, P.; Kasyutich, O.; Nolte, R.; Cornelissen, R.; Desautels, R.; van Lierop, J. Hierarchical Self-Assembly and Optical Disassembly for Controlled Switching of Magnetoferritin Nanoparticle Magnetism. *ACS Nano* **2011**, DOI: 10.1021/nn201571y.
- Kasyutich, O.; Sarua, A.; Schwarzacher, W. Bioengineered Magnetic Crystals. *J. Phys. D: Appl. Phys.* **2008**, *41*, 134022.
- Lim, J.; Lanni, C.; Evarts, E.; Lanni, F.; Tilton, R. D.; Majetich, S. A. Magnetophoresis of Nanoparticles. *ACS Nano* **2011**, *5*, 217–226.
- Xia, D.; Brueck, S. R. J. A Facile Approach to Directed Assembly of Patterns of Nanoparticles Using Interference Lithography and Spin Coating. *Nano Lett.* **2004**, *4*, 1295–1299.
- Gore, T.; Dori, Y.; Talmon, Y.; Tirrell, M.; Bianco-Peled, H. Self-Assembly of Model Collagen Peptide Amphiphiles. *Langmuir* **2001**, *17*, 5352–5360.
- Kretlow, J. D.; Mikos, A. G. Review: Mineralization of Synthetic Polymer Scaffolds for Bone Tissue Engineering. *Tissue Eng.* **2007**, *13*, 927–938.
- Shavel, A.; Rodriguez-Gonzalez, B.; Spasova, M.; Farle, M.; Liz-Marzan, L. M. Synthesis and Characterization of Iron/Iron Oxide Core–Shell Nanocubes. *Adv. Funct. Mater.* **2007**, *17*, 3870–3876.
- Kiselev, S. I.; Sankey, J. C.; Krivorotov, I. N.; Schoelkopf, R. J.; Buhrman, R. A.; Ralph, D. C. Microwave Oscillations of a Nanomagnet Driven by a Spin-Polarized Current. *Nature* **2003**, *425*, 380–383.
- Hogg, C.; Majetich, S. A.; Bain, J. A. Investigating Pattern Transfer in the Small-Gap Regime Using Electron Beam-Stabilized Nanoparticle Array Etch Masks. *IEEE Trans. Magn.* **2010**, *46*, 2307–2310.