DOI: 10.1002/anie.201006504

# Nanocrystal Self-Assembly Assisted by Oriented Attachment**

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crystal growth · nanomaterials · nanoparticles ·
oriented attachment · self-assembly

Nanoparticles with a spectrum of sizes, shapes, mass distributions (e.g. hollow, rattle-type, core–shell particles), and compositions are today routinely synthesized by a growing set of techniques involving "wet chemistry": sol–gel, solvothermal, ionothermal, and soft- and hard-templating approaches, to name a few.[1] The self- and/or directed assembly of these nanoscale building blocks into purposeful, organized superstructures with complex symmetries and tunable functionality and properties is attractive for a host of existing and emerging applications in biomedical diagnostics and sensing, electrical-energy storage, nanocomputing, optoelectronics, photonics, photovoltaics, and gas purification. The spontaneous assembly of nanostructures is also of fundamental scientific interest, as it offers uncountable possibilities for the creation of metamaterials with properties that rival those accessible from the assembly of atomic building blocks.[2] It also enables direct exploration of the interplay between all of the fundamental forces in condensed matter. Over the last decade, a torrent of new results from experiments,[3–6] as well as molecular-dynamics and Monte Carlo computer simulations of repulsive or weakly attractive particles,[4] have justified this interest by confirming that easy-to-control variables, such as particle shape, magnetization, symmetry, surface chemistry, and the concentration of depletants, can be used to independently manipulate the range and magnitude of interparticle forces that control assembly.[5] Recent results from the epitaxial growth of films even suggest that upon minor changes, rules that govern the kinetics of the assembly of atoms may be applicable to colloidal and nanoparticle building blocks.[6]

Self-assembly in a system of atoms, molecules, or particles is guided by both entropic and enthalpic interactions; the system spontaneously forms ordered phases to decrease its overall free energy. In dilute systems ordering comes at the expense of translational and orientational entropy, and for it to be maintained, long-range directional interactions are typically required. Entropic interactions caused by particle shape and excluded volume are important in assembly at a high particle concentration, but are typically too small to deflect random aggregation induced by short-range attractive forces. On the other hand, because of the large number of atoms that make up a nanoparticle, when two or more particles approach each other within distances comparable to the van der Waals radius ($R_{\mathrm{vdw}} \approx A_{\mathrm{H}} A/48\pi a k T$), enthalpic, usually attractive, forces dominate. In this equation, $A_{\mathrm{H}}$ is the Hamaker coefficient, and $A$ and $a$ are the surface area and radius of the particle, respectively. Large thermal forces ($F_{\mathrm{T}} \approx kT/a$) acting on individual particles in suspension also ensure that on average small particles approach each other in randomly selected configurations. Thus, at the high particle concentrations normally required for the assembly of coherent, ordered superstructures, these two effects conspire to produce ensembles of kinetically trapped, disordered structures that bear little, if any, resemblance to the equilibrium phases that minimize the system free energy. Fundamental processes that produce selective ordering are therefore critically required to shepherd the final stages of assembly.

Lou and co-workers report in this Issue the synthesis and simultaneous assembly of 100 nm hematite ($\alpha$-$Fe_2O_3$) nanocrystals into organized one- (1D), two- (2D), and three-dimensional (3D) superstructures.[7] Remarkably, they found that the crystallographic orientations of the ordered nanoparticle phases were in near-perfect registry across the particle–particle interface, and that the assembled structures were irreversibly linked. This type of assembly is reminiscent of crystal growth of much smaller nanocrystals by oriented attachment (OA). Discovered by Penn and Banfield over a decade ago,[8] OA has been extensively studied as a fundamental crystal-growth process. It is theorized that in the early stages of crystal growth, tiny (< 20 nm) crystallite particles aggregate spontaneously and irreversibly with almost perfectly aligned crystallographic facets. Attachment is observed primarily in one direction; that is, usually at the higher-energy surfaces, which combine to decrease the overall energy (Figure 1). Because the energetic driving force for the assembly of particles in a specific configuration is high, this process provides unusual selectivity, which gives rise to secondary single-crystal structures. As crystallization pro-

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[**] We gratefully acknowledge support from the National Science Foundation (DMR-1006323).

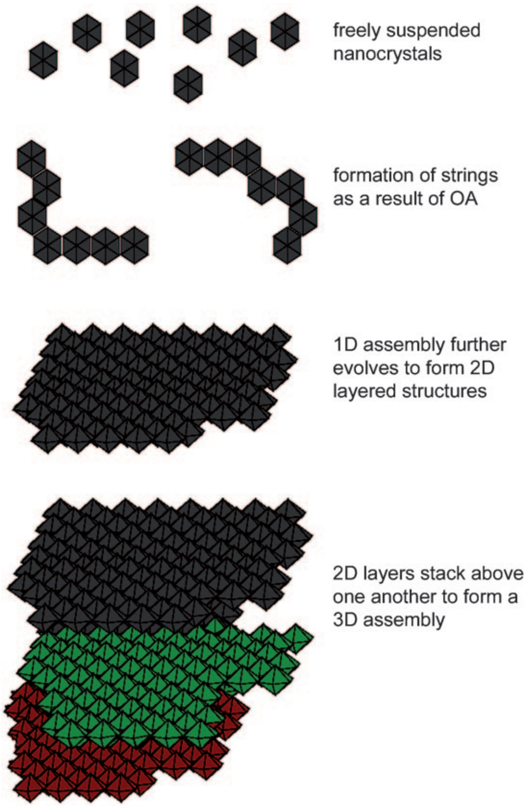

***Figure 1.*** Schematic illustration of the assembly of nanocrystals on the basis of oriented attachment. The first two figures in the schematic show the top-view of the assembling particles, and the last figure depicts a side-view of the layers produced by assembly.

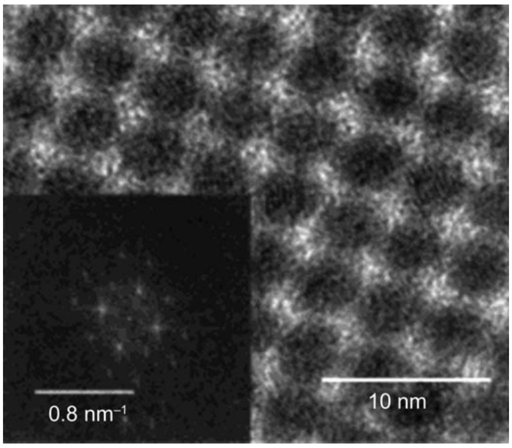

***Figure 2.*** TEM image in the (100) projection of a 3D superlattice of CdSe nanocrystals; inset: image derived by fast Fourier transform of the TEM image.[9]

ceeds, OA is generally thought to give way to Ostwald ripening, whereby larger crystals grow at the expense of smaller crystals, typically by random dissolution and the redeposition of molecular species. The study by Lou and co-workers is significant because it suggests that OA can be dominant even at larger crystal sizes and in the later stages of crystal growth. Because of its fundamental, enthalpic origin, the OA-mediated assembly of nanoscale building blocks provides a promising new tool for guiding the spontaneous assembly of even sticky metal-oxide precursors.

Most current methodologies for creating organized nanoparticle superstructures rely on pressure- and/or temperature-controlled evaporation of a suspending solvent. Ideally, this process should gradually increase the viscosity of the medium and decrease the free volume available for primary particles, so that the system slowly vitrifies, thereby locking in near-equilibrium entropy-selected structures formed in the liquid state. Capping groups tethered to the surface of primary particles can provide sufficient steric or electrostatic repulsion to control the interparticle distance and thus perfect final assembly. This method was used to create the highly ordered 3D CdSe nanocrystal superlattice structures reproduced in Figure 2.[9] Similar approaches have been employed for the self-assembly of other types of nanocrystals into quasicrystalline phases, such as plastic or glassy solids, with only short-range positional or orientational order. A variation of this scheme suitable for anisotropic shapes utilizes an adsorbed cationic surfactant to produce long-range repulsive forces between particles in solution to prevent premature aggregation.[10] A shared deficiency of these methods is that, but for the short-range entropic forces that drive the orientational and translational ordering of particle shapes of degenerate symmetry, there is no mechanism for ensuring selectivity in how nanostructures assemble. Selectivity analogous to that achieved spontaneously in assembly through OA can be engineered into nanostructures by tethering single-stranded DNA to the particles and triggering assembly by introducing multifunctional linkers bearing complementary DNA strands.[11] In analogy with OA, the high enthalpic penalty for aggregated structures bearing large numbers of unpaired nucleotides drives the system of particles to form desired, regular superstructures. A clear advantage of the approach to assembly reported by Lou and co-workers is the absence of foreign species, such as DNA, capping agents, surfactants, and polymer depletants, all of which compromise interparticle contacts and the purity of the final assembled superstructure: important properties for applications.[12]

The $\alpha$-$Fe_2O_3$ particles studied by Lou and co-workers possess hexagonal symmetry, with the sides bound by {110} surfaces. It is straightforward to show that beyond a critical particle size, $a^* > (3\,k\,T/4\pi\Delta\rho g)^{1/4} \approx 400$ nm ($\Delta\rho$ is the density difference between the particles and the suspending fluid), $\alpha$-$Fe_2O_3$ particles will spontaneously settle in aqueous solution under the influence of gravity. We hypothesize that the primary particles studied by the authors first assemble into groups of four or five, which subsequently settle and form the nuclei for the final 2D sheets and 3D stacked structures reported. For ordered structures to be formed by OA, the mechanism must be dominant even in the later stages of crystallization, which suggests that particles add to the settled nuclei one at a time to complete the process. When the primary particles were changed to rods (by increasing the concentration and temperature of the synthesis), the authors reported the production of nonuniform quasi-cubelike particles, which became more uniform as the reaction proceeded.

This last observation is typical for crystallization processes, in which Ostwald ripening results in uniformly shaped particles; however, the crystallographic orientation of adjacent rods making up the initial, nonuniform cubes were again in nearly perfect registry, reminiscent of OA. We believe that the "living" character of nanoparticles (such as those studied by Lou and co-workers) that spontaneously assemble in a medium containing a good supply of the synthesis precursors provides important advantages for the large-scale OA-mediated assembly of single-crystalline structures. Further, we predict the similar assembly of other types of "living" nanoparticle systems by OA.

Received: October 16, 2010

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[1] a) H. Goesmann, C. Feldmann, *Angew. Chem.* **2010**, *122*, 1402; *Angew. Chem. Int. Ed.* **2010**, *49*, 1362; b) X. W. Lou, L. A. Archer, Z. Yang, *Adv. Mater.* **2008**, *20*, 3987.

[2] A. van Blaaderen, R. Ruel, P. Wiltzius, *Nature* **1997**, *385*, 321; E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, *Nature* **2006**, *439*, 55.

[3] For a review of earlier studies on the spontaneous assembly of nanoparticles, see: C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

[4] S. C. Glotzer, M. J. Solomon, N. A. Kotov, *AIChE J.* **2004**, *50*, 2978.

[5] K. J. M. Bishop, C. E. Wilmer, S. Soh, B. A. Grzybowski, *Small* **2009**, *5*, 1600.

[6] R. Ganapathy, M. R. Buckley, S. J. Gerbode, I. Cohen, *Science* **2010**, *327*, 445.

[7] J. S. Chen, T. Zhu, C. M. Li, X. W. Lou, *Angew. Chem.* **2011**, *123*, 676; *Angew. Chem. Int. Ed.* **2011**, *50*, 650.

[8] J. F. Banfield, S. A. Welch, H. Z. Zhang, T. T. Ebert, R. L. Penn, *Science* **2000**, *289*, 751; R. L. Penn, J. F. Banfield, *Science* **1998**, *281*, 969; R. L. Penn, *J. Phys. Chem. B* **2004**, *108*, 12707.

[9] D. V. Talapin, E. V. Shevchenko, A. Kornowski, N. Gaponik, M. Haase, A. L. Rogach, H. Weller, *Adv. Mater.* **2001**, *13*, 1868.

[10] F. M. van der Kooij, K. Kassapidou, H. N. W. Lekkerkerker, *Nature* **2000**, *406*, 868.

[11] E. Katz, I. Willner, *Angew. Chem.* **2004**, *116*, 6166; *Angew. Chem. Int. Ed.* **2004**, *43*, 6042; S. Y. Park, A. K. Lytton-Jean, B. Lee, S. Weigand, G. C. Schatz, C. A. Mirkin, *Nature* **2008**, *451*, 553.

[12] M. V. Kovalenko, M. Scheele, D. V. Talapin, *Science* **2009**, *324*, 1417; for a Highlight, see: S. L. Brock, *Angew. Chem.* **2009**, *121*, 7620; *Angew. Chem. Int. Ed.* **2009**, *48*, 7484.