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Letter to the Editor

Controlled self-assembly of colloidal cobalt nanocrystals

There is growing interest in organizing materials on the nanometer scale for fundamental investigations [1–3] and novel technological applications [5,6]. One of the most promising routes to create highly ordered structures on the nanometer scale is by the self-assembly of nanoscale building blocks comprised of colloidal nanocrystals [7,8]. However, the mechanisms influencing the self-assembly of such nanocrystals are not understood [9] and there is a critical need to develop general approaches for predicting and controlling this behavior. Here, using surfactant-stabilized Co nanocrystals [10] with narrow size distributions and controlled shapes as building blocks, we describe our ability to finely tune their self-assembled arrays. We can selectively achieve square packing, hexagonal close packing, linear chains, arrays spatially segregated as a function of particle size and lyotropic liquid-crystal-like arrays with orientation order. This richness in self-assembly is obtained in a single system as a function of size and shape, and in which one of a set of competing forces (steric, van der Waals, depletion, entropy or magnetostatic) dominates to determine the resulting organization.

It is well known that colloidal nanoparticles suspended in a liquid will spontaneously self-assemble into highly ordered, close-packed hexagonal arrays when their packing densities approach a critical value [1,11]. This process is understood in terms of an entropy-driven, first order, liquid–solid phase transition in the limit of a hard sphere system [2,12]. Similar experiments, however, performed in microgravity [13] reveal significant differences from terrestrial experiments suggesting the possibility of using competing forces of similar magnitudes to influence the self-assembly process. In addition to such solvent evaporation crystallization [4,6], close-packed planar crystal arrays are also formed by other methods such as coulombic interaction [7], and molecular cross-linking [5]. The only reproducible approach to obtain non-close-packed arrays was by the use of template-directed colloidal crystallization using patterned substrates [14,15]. Our systematic investigation of the behavior of cobalt nanocrystals via the evaporation rate gradient method[1] suggests that close-packed hexagonal arrays are not always the case and the details of the self-assembled arrays can be selectively controlled.

We synthesize cobalt nanoparticles by a modified form of the La Mer method [16] involving the injection of organometallic precursors into a hot coordinating solvent containing a surfactant mixture under inert atmosphere. This produces a temporally discrete but homogeneous nucleation event followed by growth in solution. The surfactant mixture dynamically coats the particles, allows for monomer exchange, protects the nanocrystals from being oxidized and controls the

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[1] Spherical cobalt particles are synthesized by injecting stock solution (0.54 g $Co_2(CO)_8$ dissolved in 3 ml 1,2-dichlorobenzene) into refluxing 1,2-dichlorobenzene at 182°C in the presence of 0.2 ml oleic acid and 0.1 g TOPO. Disks are prepared in a similar manner except 0.34 g linear amines are substituted for TOPO. We are developing a precipitation technique that is a variation of the solvent–non-solvent pair method, in which mixtures of solvents (toluene, hexane, dichlorobenzene) and non-solvents (methanol, butanol) with different boiling temperatures produce an evaporation rate gradient. This technique allows particles to remain in solution with sufficient thermal energy to slowly form highly ordered structures. The non-solvent mixture is added drop wise to a dilute solution of particles, which precipitate onto a SiO or amorphous carbon TEM film. This method produces 2D arrays most of the time.

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minimum interparticle distance. Further, if appropriate surfactants that preferentially bond to specific crystallographic surfaces of the growing crystal can be identified, the shape of the nanocrystals can be reproducibly controlled [10]. Both ε-Co[2] and HCP-Co are obtained from this synthesis procedure. The crystal structure of the Co nanocrystals was investigated by X-ray and electron diffraction, and their arrays were observed by high-resolution electron microscopy. Magnetic properties were determined by vibrating sample magnetometry (VSM).[3]

Self-organization of the particles into ordered monolayer on surfaces is driven by a combination of evaporation, convection and inter-particle interaction forces. As the evaporation front passes over a hydrophilic surface at a controlled rate, the particles dispersed in solution are pulled towards the drying front by convection and then deposited there as the drying front becomes very thin. Capillary forces subsequently pull the particles together into ordered arrays. However, arrays of our cobalt nanocrystals exhibit a surprising richness in form and symmetry as a function of their size, size-distribution and shape. Here, we report the different arrays observed and interpret our results in terms of critical, but well-defined, interparticle interactions. These include the long-range attractive van der Waals forces due to polarizable metal particles, the magnetostatic interactions between magnetic dipoles, steric stabilization arising from the surfactant coatings on the nanoparticle surfaces and entropy effects.

The magnetic behavior of cobalt nanocrystals, including their interactions, plays an important role in determining their self-assembly. Small (diameter, $d < 70$ nm) [18] Co nanocrystals are single domain, i.e. the exchange interaction couples all the atomic magnetic moments, and they can be considered as a large magnetic dipole. In each nanocrystal this magnetic dipole may favor specific crystallographic orientation depending on its magnetocrystalline anisotropy (six-fold for cubic ε-Co and uniaxial for HCP-Co). The magnetocrystalline energy is a product (kV) of the anisotropy constant (k) and the nanocrystal volume (V). When compared to the thermal energy, $k_{\mathrm{B}}T$ it determines the magnetic stability of the nanocrystals; typically the magnetic relaxation time depends exponentially on the particle volume [19]. As a result, at room temperature, particles smaller than a critical size (diameter < 10 nm for Co) have magnetic dipole moments that are free to rotate in any direction (superparamagnetic on the time scale of routine SQUID measurements); in larger particles the magnetic dipole moment is fixed along the easy directions of anisotropy (ferromagnetic). Such ferromagnetic particles, with time constants for rotation in solution shorter than the time for self-organization, favor arrangements that minimize their magneto-static energy arising from the interaction of their magnetic dipoles.

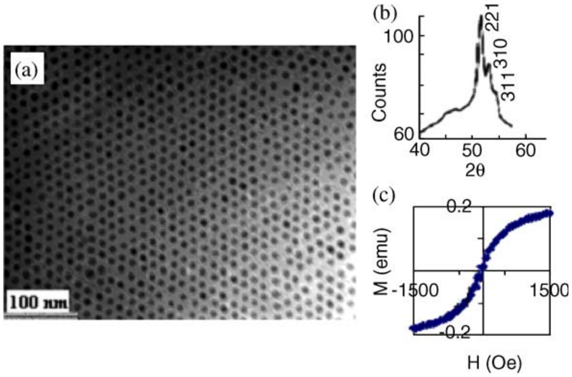

Fig. 1. Hexagonal close-packed 2D lattice of 8–10 nm spherical nanocrystals: (a) TEM image; (b) XRD $\theta - 2\theta$ scan, peaks correlate with ε-cobalt; and (c) closed hysteresis loop indicates superparamagnetic behavior. In this case, a hard-sphere model applies and the hexagonal arrangement results from a first-order phase transition as a function of concentration.

Superparamagnetic ε-Co nanocrystals (diameter ~8–9 nm) assemble into hexagonal close packed 2D arrays (Fig. 1a). This behavior may be explained by the classical first-order phase transition (i.e. melting and freezing) as a function of concentration (thermodynamic variable). The total internal energy for this system consists of the sum

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[2] Space group $P4_132$; β-Mn structure, with a cubic unit cell and $a_0 \sim 0.61$ nm (also see Ref. [17]).

[3] The magnetic measurements are done in powder form at room temperature using VSM. It is assumed that the powders are randomly dispersed, but have the same size distribution as observed in the TEM images.

of the van der Waals, steric repulsion, magnetostatic energy and other second-order terms that include hydrophobic attraction between surfactants. The hydrophobic attraction is negligible in nonpolar solvents, and at room temperature the magnetostatic energy between superparamagnetic particles is also negligible. A preliminary calculation shows that $k_B T$ is on the same order of magnitude as the van der Waals potential. The steric repulsion term (also of the order of $k_B T$) will further reduce the total internal energy. It is then reasonable to assume that $k_B T$ is larger than the total internal energy and the self-assembly of the system can be approximated by the hard-sphere model [1]. Typically, as the solvent evaporates and the volume fraction [12] increases, the particles freeze into the well-known hexagonally ordered arrays.

With rapidly increasing surface to volume ratio we observe that this hard-sphere approximation breaks down for very small ε-Co nanocrystals (~ 4 nm). Their self-assembly is dominated by the steric forces between the surfactant molecules on their surface and leads to the formation of square nanoparticle arrays (Fig. 2a). Oleic acid, with a 18 carbon atom backbone (chain length 2.3 nm), was the surfactant used for stabilization. The observed interparticle separation (2.5 nm) for these small crystallites is less than twice the theoretical chain length of oleic acid; at equilibrium separation the surfactant tails between neighboring particles are compressed (interpenetrate by 2.1 nm)—a process that would decrease the entropy of the system. For particle sizes of interest and inter-particle distances observed, four-fold coordination is favored over six-fold coordination to minimize the surfactant-overlap volume. An alternative, but less-likely explanation involves the role of the poyhedral shapes [20], along low symmetry directions such as (6 2 5), on the nanocrystal assembly.

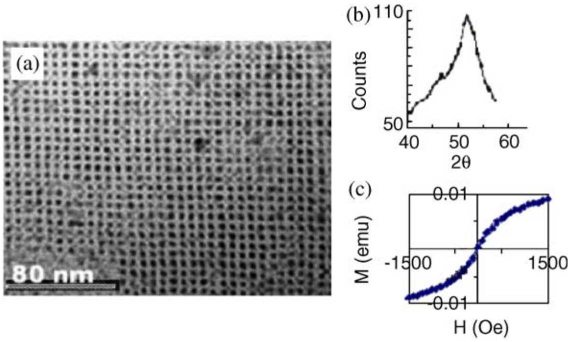

Fig. 2. Two-dimensional square lattice of 4 nm spherical nanocrystals: (a) TEM image; (b) XRD $\theta - 2\theta$ scan showing size effect peak broadening, but peak position indicates ε-cobalt; and (c) closed hysteresis loop suggests superparamagnetic behavior. The hard-sphere model breaks down, leading to significant surfactant overlap. A square arrangement minimizes the overlap volume and dominates the self-assembly process.

On the other hand, a bimodal combination of 6 and 12 nm particles leads to a controlled entropic attraction between larger particles [21]. If the sums of the volumes of small spheres and large spheres are comparable, then the entropy of the small spheres will dominate the system. In principle, to first order, the larger size spheres will then adopt those configurations that maximize the entropy of the small spheres. This can be accomplished either if the large spheres touch each other or if the large spheres preferentially touch the surface. The former is akin to a fictitious attractive force between larger particles (also called depletion or excluded-volume force) and the latter is equivalent to a preferential "wetting" of the surface by the larger particle. This simple argument[4] predicts a size-dependent segregation of the ordered arrays with the smaller size nanocrystals delegated to the periphery of the hexagonal array of the larger particles. This is indeed observed for the case of our ε-Co nanocrystals with a bimodal size-distribution (Fig. 3a). Such entropic effects likely contribute to how a wide size-distribution of disks also assembles with larger discs attracted to the center of the array (Fig. 3b).

Larger ε-Co particles (~ 18 nm) are ferromagnetic at room temperature and show (Fig. 4c) open hysteresis loops. Consequently, the collection of particles (each considered as a dipole) are observed to self-organize such that the net magneto-static energy, which scales as d^6, of the array is

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[4] Alternatively, for heterogeneous mixtures of colloids in solution, size-selective precipitation from kinetic considerations could also contribute to such nanocrystal segregation. Controlled precipitation experiments have been initiated to determine under which conditions, if any, such kinetic effects become important.

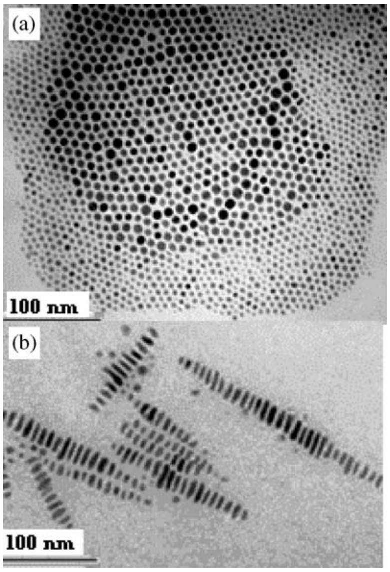

Fig. 3. TEM images of nanocrystals with non-uniform size distributions: (a) spherical nanocrystals; and (b) nanodisks—the shape of the nanocrystals were confirmed independently by tilting and high-resolution electron microscopy. In this case the entropy-driven depletion force dominates leading to a spatial separation as a function of size. Note that this is independent of the shape of the nanocrystals.

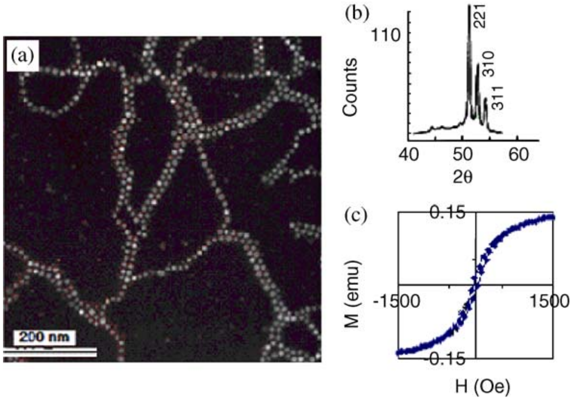

Fig. 4. Chains of 18 nm spherical nanocrystals: (a) TEM image; (b) XRD $\theta-2\theta$ scan, peaks correlate with ε-cobalt; and (c) open hysteresis loop suggests ferromagnetic behavior. The magnetostatic interaction between ferromagnetic particles determines the self-assembly.

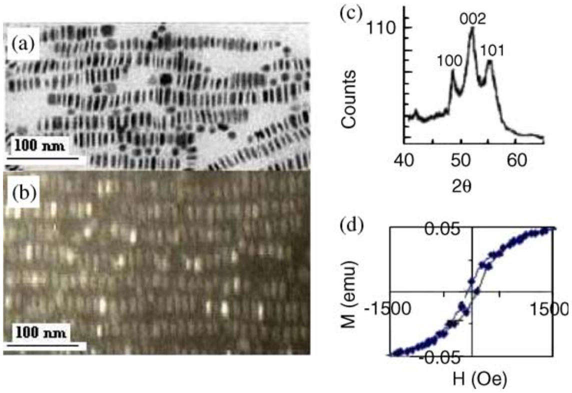

Fig. 5. Arrays of nanodisks (5 nm thick, 20 nm diameter) (a)(b) TEM images. Orientation order increases with concentration, i.e. lyotropic liquid crystal behavior. (c) XRD $\theta-2\theta$ scan, peaks correlate with HCP cobalt (d) Open hysteresis loop suggests ferromagnetic behavior. The magnetostatic energy is a minimum when the neighboring disks lie face to face.

minimized. The dipoles are observed to assemble in a tip to tail linear chain orientation; further, the chains fold into loops in order to close the stray magnetic field lines. Preliminary electron holography measurements (Gau, Shindo, Bao and Krishnan, unpublished) suggest that the field lines are channeled parallel to the particle chains, confirming that the magnetostatic forces dominate and lead to the resulting self-assembled linear arrays.

Shape and magnetocrystalline anisotropy compete in HCP-cobalt to determine the resulting magnetization direction in disk shaped particles. Our calculations suggest that shape anisotropy is dominant and magnetization lies in the plane of the disk when the thickness to diameter ratio is less than one-half. The magneto-static energy is then minimized when neighboring particles have antiparallel spins, resulting in the particle array shown in Figs. 5a, b and 3b. Hydrophobic interaction between surfactant tails tends to draw them together. Therefore, disks will stack face to face in order to maximize contact between surfactant tails, thus minimizing exposure to air. These anisotropic nanodisks exhibit lyotropic liquid crystal behavior and show an increase in orientational order with increasing concentration (Figs. 5a and b).

In summary, we have demonstrated that a rich set of self-assembled arrays can be obtained from a *single* component system by a controlled variation of nanocrystal size, shape and inter-particle interactions. Moreover, in a nanocrystal system in which a number of weak but competing interaction forces exist, by selecting appropriate conditions in which one of them dominates we can achieve significant control and diversity in the nature of the self-assembled arrays. This principle could serve as a fundamental guideline for the controlled self-assembly of nanoparticle arrays with implications for emerging magnetic applications, such as data storage and spin electronics.

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