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Controlled self-assembly of colloidal cobalt nanocrystals mediated by magnetic interactions

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Abstract

We demonstrate the possibility of obtaining a rich set of self-assembled arrays from a *single* component cobalt nanocrystal (NC) system by a controlled variation of size, shape and inter-particle interactions. By selecting appropriate conditions in which one of a set of weak but competing interaction forces (steric, van der Waals, depletion, or magnetostatic) dominates we can reproducibly achieve a wide range of nanocrystal arrays. This includes hexagonal and square arrays, arrays spatially segregated by size, linear chains and lyotropic crystals exhibiting increased orientation order as a function of concentration.

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Size-dependent scaling laws and the magnetic behavior of small particles and nanostructured assemblies, as a function of size, shape, dimensionality and inter-particle interactions are increasingly of fundamental and technological interest. In this paper, we present a summary of our recent results on the synthesis of mono-disperse, metallic, passivated cobalt nanocrystals with good size/shape control; their self-organization as a function of size, size-distribution and shape, and their isolated and collective magnetic behavior.

The Cobalt particles are synthesized by a modified form of the La Mer method [1], which involves the rapid injection of organometallic precursors into a hot coordinating solvent containing a surfactant mixture under inert atmosphere. This produces a temporally discreet, homogeneous nucleation event followed by subsequent growth in solution. The surfactant mixture dynamically coats the particles, allows for monomer exchange leading to size-selective focusing, prevents the nanocrystals from being oxidized and controls the 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 [2]. Both ε-Co (β-Mn structure) and HCP-Co are obtained from this synthesis procedure.

The magnetic behavior of cobalt nanocrystals, including their interactions, plays an important role in determining their self-assembly. Small (diameter, $d < 70\,\mathrm{nm}$) [3] 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_BT it determines the magnetic stability of the nanocrystals; typically, the magnetic relaxation time depends exponentially on the particle volume [4]. As a result, at room temperature, particles smaller than a critical size (diameter < 10 nm for Co) have magnetic dipole

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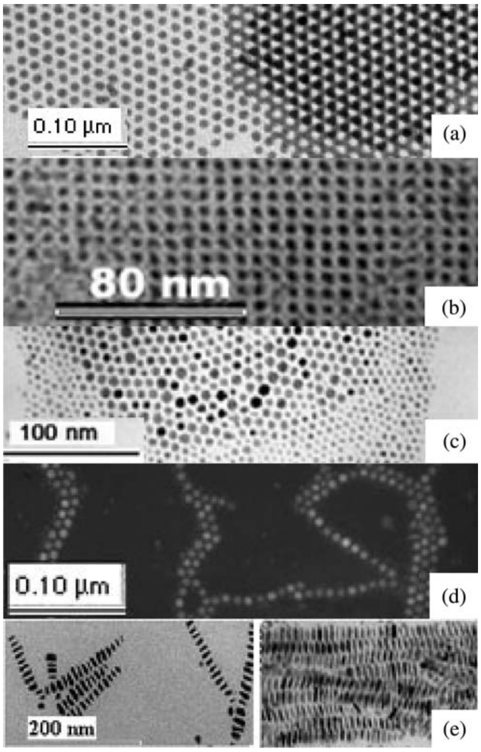

Fig. 1. TEM images of cobalt nanoparticles: (a) hexagonal close packed array, (b) square packed array, (c) bimodal size distribution, (d) linear chains of larger spheres (about 18 nm), and (e) lyotropic ordering of disk-shaped particles; low concentration (left) and high concentration (right).

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.

The self-organization of the particles is dependent on their size, size distribution, shape and inter-particle interactions [5,6]. Cobalt nanocrystals $\sim$8–9 nm in diameter (ε-Co and super-paramagnetic) behave as hard spheres and show a classical first-order phase transition (i.e. melting and freezing) as a function of concentration (thermodynamic variable). They assemble in a close-packed two-dimensional hexagonal lattice (Fig. 1a). With rapidly increasing surface to volume ratio we observe that this hard-sphere approximation breaks down for very small ε-Co nanocrystals ($\sim$4 nm). Their self-assembly is dominated by the steric forces between the surfactant molecules on their surface leading to a square lattice (Fig. 1b). On the other hand, if these two sizes are combined to give a bimodal-size distribution the vibrational entropy of the system dominates. The resultant "depletion" forces lead to a preferential wetting of the surface by the larger particles (Fig. 1c). Larger ε-Co particles ($\sim$18 nm) are ferromagnetic at room temperature and show open hysteresis loops. These nanocrystals form linear chains and closed loops (Fig. 1d) to minimize their magnetostatic energy. Preliminary electron holography measurements [7] 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. Disk shaped facetted particles (HCP-Co, 5 × 20 nm) also form linear arrays with the magnetization between neighboring nanocrystals being antiparallel (Fig. 1e). Hydrophobic interaction between surfactant tails tends to draw them together. Therefore, disks 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.

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