

Synthesis, self-assembly and magnetism of surfactant-stabilized nanocrystals

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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. Both metal and oxide nanoparticles are synthesized by the rapid injection of organometallic precursors into a hot coordinating solvent containing a surfactant mixture under inert atmosphere [1]. 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 metal 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. Recently, we have further developed this synthesis method to fabricate a variety of magnetic nanoparticles with desirable structures and controlled properties [2]. Different morphologies are achieved by controlling the particles during nucleation and growth stage. Particular examples are high K_u alloy nanoparticles for ultra-high density magnetic data storage, biocompatible air-stable gold-coated core-shell nanoparticles, and cobalt nanoparticles with controlled crystal defects. The morphology of binary particles is dependent on their bulk thermodynamics--for immiscible heterogeneous systems (Co-Au) core-shell structures are obtained whilst miscible systems (Fe-Pt) lead to alloy nanoparticles [3]. Relative stability of cobalt nanocrystals is analyzed using temperature dependences of DC magnetic susceptibility. The method is based on the observation that with particle oxidation, an anomalous peak appears at 8 K in zero field-cooled magnetization measurements. This peak is not associated with the volume dependent blocking peak. It is found that the surfactant protective layer is more important for long-term stability at room temperature, while the high temperature oxidation rate is controlled by the crystal quality of nanoparticles [4].

The self-organization of the particles is dependent on their size, size distribution, shape and inter-particle interactions [5]. 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. For the simplest case (ϵ -Co nanospheres, 11 nm dia, super-paramagnetic at room temperature) a hexagonal arrangement of NCs is observed in transmission electron microscope (TEM) images when precipitated from solution onto carbon films. Small angle x-ray scattering (SAXS) measurements were also performed on cobalt nanospheres randomly dispersed in solution and assembled on glass substrates. Structure factor contribution to the intensity profile agrees well with a quasi-random model for scattering from a face centered cubic (FCC) superlattice composed of uniform radius cobalt spheres. The measured nearest neighbor interparticle spacing, 14.1 nm, agrees to within 2% of the predicted value of

14.4 nm based on a free energy model that governs the self-assembly of the nanoparticle system. Superlattice grain diameter, or structural correlation length, is related to peak broadening according to the Scherrer equation. The analysis is complicated by the presence of two theoretical scattering maxima within the first experimental peak, but yields a value of approximately 70 nm for the correlation distance [6].

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 leading to a square lattice. 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. Larger ϵ -Co particles (~ 18 nm) are ferromagnetic at room temperature and show open hysteresis loops. These nanocrystals form linear chains and closed loops to minimize their magnetostatic energy. Preliminary electron holography measurements 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 [7]. Disk shaped faceted particles (hcp-Co, 5×20 nm) also form linear arrays with the magnetization between neighboring nanocrystals being antiparallel. 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.

Measurement of the variation of relaxation frequency of Brownian rotation of magnetic nanoparticles in a ferrofluid due to binding of organic molecules to the particles has been proposed as a tool for detection of biomolecules in solution. This method makes use of the dependence of relaxation time τ_r on the particle effective hydrodynamic radius r , which increases with attaching the molecules $\tau_r = 4\pi r^3 \eta / k_B T$ (η is the viscosity). Recently, we have demonstrated that this simple idea can be complicated by relaxation due to surface friction between the bound molecules on neighboring particles [8]. On the other hand, the low frequency peak appearing due to surface friction can itself be used in biosensing as an indicator of the attached molecules [9].

References:

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