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Self-Assembly of Cobalt Nanoparticle Rings

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Assemblies of metallic and inorganic nanoparticles are well-known to yield collective physical properties dependent on particle size, spacing, and higher-order structure.[1,2] Methods for controlling the latter two parameters are limited and represent an important challenge in nanoscale materials synthesis. Here we report that weakly ferromagnetic cobalt nanoparticles can self-assemble into braceletlike rings with discrete particle count when dispersed by *C*-undecylcalix[4]resorcinarene (**1**). These nanoparticle "bracelets" are distinct from the micrometer-sized rings created by rapidly evaporating films of dispersed nanoparticles,[3,4] both with regard to ring size (typically 5−12 particles and 50−100 nm in diameter, see Figure 1a) and to their mechanism of assembly.

Cobalt nanoparticles were prepared by the thermolysis of $Co_2(CO)_8$ in hot toluene solutions containing resorcinarene tetraphosphonite **2**.[5,6] Fractionation by several cycles of magnetically induced precipitation and redispersion under ambient conditions ultimately yielded Co nanoparticles with a size distribution of 27 ± 4 nm. A powder sample exhibited weak ferromagnetism at 295 K as determined by SQUID magnetometry ($M_S = 95$ emu/g, $M_R/M_S = 0.13$, $H_C = 175$ Oe).[6] Energy-filtered transmission electron microscopy (EFTEM)[7] revealed that the Co nanoparticles were encapsulated by a thin (3−4 nm) but stable oxide layer (see Figure 1b). Although the ferromagnetic properties of the Co particles may be compromised by exchange anisotropy with the antiferromagnetic CoO shell,[8] the size of the Co core allows the nanoparticles to act effectively as single-domain magnetic dipoles at room temperature.[9]

The Co nanoparticles formed stable suspensions in toluene or CH_2Cl_2 (10^{13} particles/mL, ~0.015% v/v) when dispersed in the presence of resorcinarene **1**. Nanoparticles were fully dispersed by sonication and then cast and dried onto carbon-coated TEM grids by a standardized procedure.[3c,6] Co nanoparticles dispersed with minimal surfactant ($<10^{-6}$ M) produced only densely packed particle films when deposited in this manner, demonstrating that van der Waals attractive forces drive aggregation in the limit of low viscosity.[10] In comparison, dispersions containing resorcinarene **1** (10^{-6}−10^{-3} M) invariably produced nanoparticle bracelets, as well as other aggregate structures such as short chains or rafts of densely packed particles (see Figure 2).[11] Further aggregation is presumed to have been arrested by the increasing viscosity of the nonvolatile surfactant film, with subsequent pinning of the nanoparticles to the substrate. The residual wetting layer becomes viscous at an earlier stage of drying with higher initial concentrations of **1**, providing "snapshots" of nanoparticles in various phases of aggregation. Indeed, increasing the surfactant volume fraction from 0.001 to 0.1% resulted in a greater proportion of both nanoparticle chains and bracelets relative to particle rafts.[6] We therefore consider these self-assembled structures to be kinetically stabilized by the presence of the surfactant.[11]

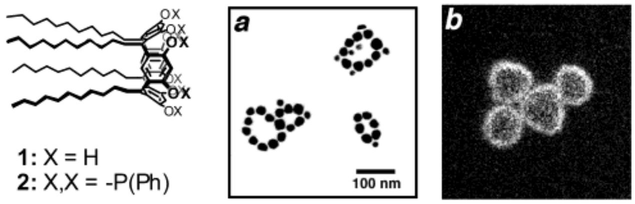

Figure 1. (a) TEM image (Philips EM-400, 80 kV) of Co nanoparticle "bracelets" dispersed in toluene with resorcinarene **1**. Sample was prepared by wetting a carbon-coated Cu grid with a thin layer of nanoparticle dispersion and drying in air.[6] (b) EFTEM image (JEOL 2010-F) of 27 ± 4 nm Co particles showing O distribution. The oxide layer is at least one year old.

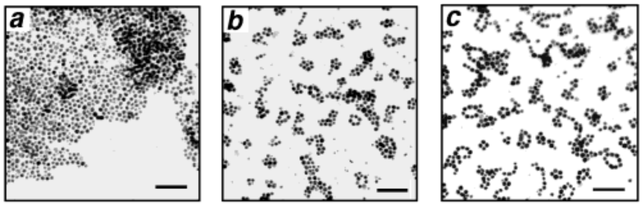

Figure 2. TEM images (Philips EM-400, 80 kV) of 27 ± 4 nm Co particles dispersed in toluene at different initial concentrations of **1**: (a) $<10^{-6}$ M, (b) 10^{-5} M, (c) 10^{-3} M. Scale bar = 200 nm.

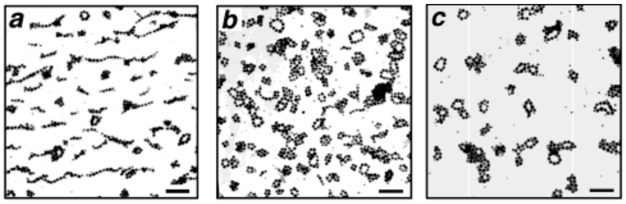

Figure 3. TEM images (Philips EM-400, 80 kV) of Co nanoparticle aggregate structures formed in the presence of an external magnetic field (225 G). 27 ± 4 nm Co particles (10^{13} particles/mL) were dispersed in toluene containing **1** (10^{-4} M) and cast onto carbon-coated TEM grids under the following conditions: (a) exposure to an external magnetic field during deposition and drying; (b) magnetic field exposure for 90 s, then sonication for 90 s prior to deposition; (c) magnetic field exposure for 70 min, then aged for 1 week at room temperature prior to deposition. Scale bar = 200 nm.

We have strong evidence that chain and bracelet formation are directed by the magnetic moments of the Co nanoparticles, whose dipolar interactions compete with nondirectional van der Waals interactions at close range. Some insights were obtained by exposing resorcinarene-stabilized Co nanoparticles to a magnetic field (225 G), which enhances the strength of magnetic dipole interactions. Nanoparticles cast and dried under a magnetic field with minimal agitation were deposited as both oriented chains and bracelets (see Figure 3a). Longer exposures resulted in extensive chaining,[6] but sonication or simply aging of the suspension prior to deposition restored a high bracelet number density (see Figure 3b, c). These results indicate that bracelet self-assembly occurs in solution, and

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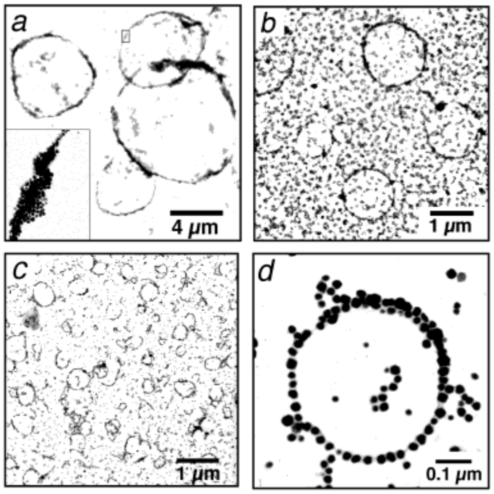

Figure 4. TEM images (Philips EM-400, 80 kV) of mesoscopic nanoparticle rings. 27 ± 4 nm Co particles (10^{13} particles/mL) dispersed in CH_2Cl_2 at different initial concentrations of **1**: (a) $<10^{-6}$ M (inset 10× magnification), (b) 10^{-5} M, (c) 10^{-3} M. (d) Submicrometer nanoparticle ring approaching single-particle annular thickness, produced at $[\mathbf{1}]_0 = 10^{-4}$ M.

can be produced by chain degradation. The discrete size range of these ensembles is most likely regulated by a balance between the enthalpic gain from magnetic nanoparticle assembly and entropic loss, analogous to the thermodynamic equilibrium of forces governing the self-assembly of supramolecular aggregates.[12]

Evaporation-driven instabilities such as hole nucleation[13] and Rayleigh−Bénard convection[14] are not responsible for bracelet formation, although they can be used to create larger mesoscopic rings. Co nanoparticles cast from CH_2Cl_2 dispersions under dissipative conditions produced a rich variety of ringlike assemblies, whose formations were highly dependent on initial concentrations of **1** (see Figure 4). Deposition with minimal surfactant resulted in large (2−10 μm), nonuniform rings with walls several particles thick and 1−2 layers high. Deposition at low concentrations of resorcinarene **1** produced smaller (0.5−2.0 μm), more symmetrical multiwalled rings, similar to those created from dispersions of other nanoparticulate materials.[3,15] Both the diameters and annular widths of these rings decreased with increasing solute volume fractions, in accord with hole nucleation theory.[13] Rings with single-particle annular thickness are observed at surfactant concentrations of 10^{-4}−10^{-3} M (0.01−0.1% v/v); however, a close examination by TEM reveals that individual particles are not spaced closely together compared to those in the nanoparticle bracelets. This demonstrates that magnetic dipolar interactions do not play a dominant role in the formation of these larger rings.

In conclusion, nanoparticle rings can be formed by two different mechanisms: dipole-directed self-assembly and evaporation-driven hole formation in viscous wetting layers. Although the two mechanisms are disparate in this study, they may prove to be synergetic in the assembly of well-defined rings from larger magnetic nanoparticles, whose cooperative dipolar interactions might otherwise produce extended chains.[5a] Further studies will be needed for defining conditions to produce rings in high yield and narrow size distributions. Using self-assembly to control the dimensions of Co nanoparticle rings may then provide a means for tuning their collective magnetic configurations, such as those recently described for cobalt ring mesostructures produced by lithographic methods.[16]

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Supporting Information Available: Synthesis and characterization of resorcinarene **2** and Co nanoparticles, and detailed deposition procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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