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Polymer-Coated Ferromagnetic Colloids from Well-Defined Macromolecular Surfactants and Assembly into Nanoparticle Chains

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The functionalization and organization of magnetic nanoparticles into complex mesostructured assemblies has generated considerable interest as a novel approach to materials synthesis.[1] Ferromagnetic colloids are intriguing building blocks for self- or field-induced assembly into one-dimensional (1-D) nanostructures due to the dipolar associations between inorganic nanoparticles.[2] Our motivation in this area is to utilize the selective dipolar associations between ferromagnetic colloids as a novel approach for controlled nanoparticle assembly.

A number of groups have reported the incorporation of organic polymers to magnetic colloids using surface-initiated controlled polymerizations,[3] in situ nanoparticle reactions, or block copolymer templates.[4] The preparation of polymer-coated ferromagnetic nanoparticles is more challenging, as high-temperature annealing steps are often required to convert superparamagnetic colloids into ferromagnetic phases.[5] A few examples of polymer-coated ferromagnetic nanoparticles of metallic cobalt (Co)[2a,4a] or iron[6] have been reported; however, methodologies to synthesize well-defined nanocomposite colloids of uniform size and tunable magnetic properties have not been extensively developed.

Herein, we describe the synthesis and characterization of polymer-coated ferromagnetic nanoparticles that organize into extended one-dimensional assemblies when cast onto supporting surfaces. Controlled radical polymerization, specifically, nitroxide-mediated polymerizations,[7] enables the preparation of polymeric surfactants which were used as shells to coat ferromagnetic cobalt colloids and ensure uniformity of the particle size. By control of the macromolecular structure and functionality, we demonstrate for the first time the use of well-defined end-functional polymers to prepare polystyrene-coated ferromagnetic cobalt colloids. The polymer shell imparts long-term colloidal stability to magnetic dispersions in solution, and in the solid state, forms a glassy coating that locks in the 1-D structure of assembled nanoparticle chains through interdigitation of polystyrene outer layers.

Polystyrene (PS)-coated cobalt nanoparticles were synthesized by the thermolysis of dicobaltoctacarbonyl (Co_2CO_8) in the presence of end-functional polymeric surfactants in refluxing 1,2-dichlorobenzene. Two different pS surfactants, **3** and **4** ($M_n = 5000$ g/mol; $M_w/M_n = 1.09$), containing either a benzylamine or dioctylphosphine oxide[8] end group were synthesized to mimic the small molecule surfactant system developed by Alivisatos et al.,[9] using aliphatic amines and trioctylphosphine oxide (TOPO) (Scheme 1).[10] A mixture of amine and phosphine oxide PS surfactants (4:1 wt ratio) was then used in the thermolysis of Co_2CO_8 to prepare polymer-coated cobalt nanoparticles, where the ligating end group passivated the colloidal surface. The combination of both amine and phosphine oxide ligands was necessary to yield uniform ferromagnetic nanoparticles, which is in agreement with similar studies using small molecule surfactants.[5] Furthermore, ferromagnetic cobalt colloids were obtained for pS surfactant systems despite variation of the molar mass in the range of 2000−9000 g/mol. However, end-functional polymers possessing $M_n = 5000$ g/mol afforded the optimal combination of uniform particle size and long-term colloidal stability.[10]

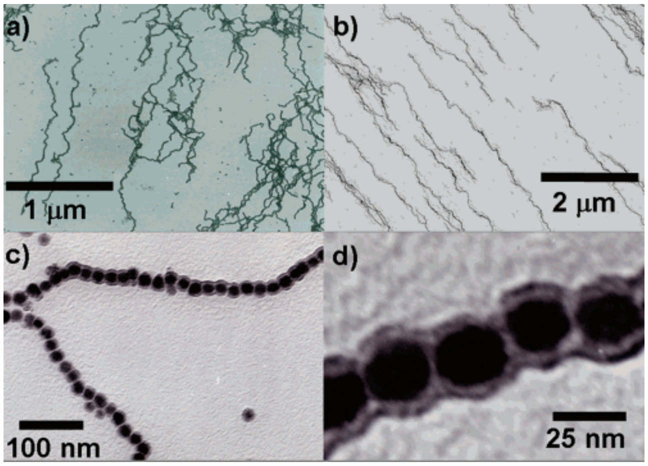
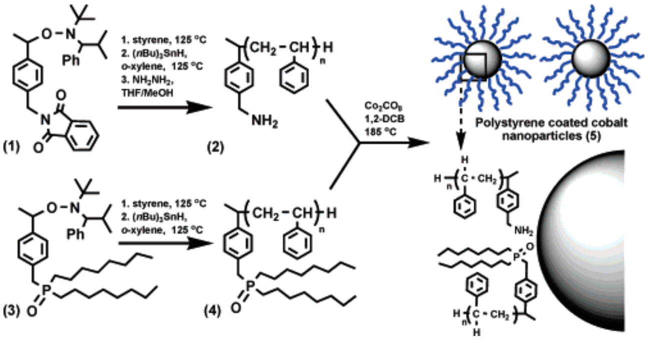


Figure 1. TEM images of ferromagnetic pS-coated cobalt nanoparticles (a) self-assembled by deposition from toluene dispersions onto carbon-coated copper grids, (b) cast from toluene dispersion and aligned under a magnetic field (100 mT), (c) self-assembled single nanoparticle chains, and (d) high-magnification image visualizing cobalt colloidal core (dark center) and pS surfactant shell (light halo).

Scheme 1. Synthesis of Polystyrenic Surfactants and Cobalt Nanoparticles



These polymer-coated cobalt nanoparticles (pS−Co) were then characterized using transmission electron microscopy (TEM), atomic force microscopy (AFM), and magnetic force microscopy

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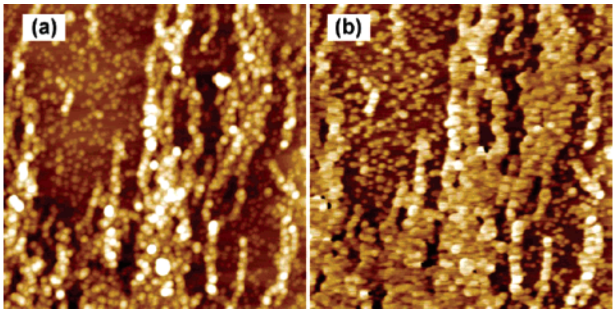

Figure 2. Topographical and magnetic images (size 5 × 5 μm^2) of pS−cobalt nanoparticles cast onto carbon-coated mica. AFM (a); MFM (b).

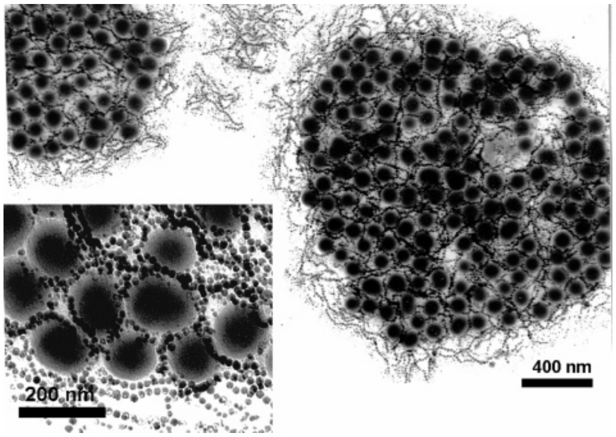

Figure 3. TEM image of binary assemblies composed of pS-coated cobalt nanoparticles and SiO_2 beads.

(MFM) to determine particle size and morphology of magnetic colloids and nanoparticle chains. Low-magnification TEM images of colloids cast onto surfaces reveal the formation of uniform colloids organizing into extended nanoparticle chains spanning several microns in length (Figure 1a). These chains are easily aligned by deposition of the colloidal dispersion in the presence of weak magnetic fields (100 mT) (Figure 1b). TEM images of these 1-D chains at higher magnification clearly demonstrate the presence of individual cobalt nanoparticles ($D_{particle} = 15 \pm 1.5$ nm) surrounded by a halo of pS (shell thickness = 2.0 nm, Figure 1c,d). The retention of the polymer coating on the cobalt colloid was confirmed using X-ray photoelectron spectroscopy, as evidenced by the characteristic signature of pS with peaks at 284 and 288 eV.[10]

Aligned chains of nanoparticles were also clearly evident in topographical AFM (Figure 2a) and MFM (Figure 2b) images (cf. Supporting Information). All particles in MFM images appeared brighter than the nearby substrate surface, and the observed contrast did not depend on the direction of tip magnetization. Such behavior can be viewed as an indication that nanoparticle dipole moments were practically parallel to the surface.[10]

Vibrating sample magnetometry (VSM) confirmed that these hybrid materials were weakly ferromagnetic at room temperature ($M_s = 38$ emu/g, $H_c = 100$ Oe) and strongly ferromagnetic at 40 K ($M_s = 38$ emu/g; $H_c = 2000$ Oe). Significant enhancement of the magnetic coercivity ($H_c = 340$ Oe) was observed by aligning nanoparticle chains under a weak magnetic field at 300 K due to the coupling of magnetic dipole moments along the 1-D assembly.[10] X-ray diffraction (XRD) of pS-coated magnetic nanoparticles indicated the formation of the face centered cubic phase of cobalt and the presence of a thin cobalt oxide (CoO) passivating layer around the metal core. The polymer-coated colloids were observed to be stable to further oxidation over a period of several weeks to months, as confirmed from VSM and XRD.

To illustrate the potential of 1-D nanoparticle chains for bottom-up assembly, ferromagnetic pS−cobalt colloids were blended with silica beads ($D = 172$ nm) and cast onto TEM grids. The formation of micron-sized assemblies composed of isolated SiO_2 colloids dispersed in a matrix of pS−cobalt nanoparticle chains was imaged using TEM (Figure 3). Nanoparticle chains were observed to organize around larger silica inclusions. While the overall size of the cobalt−SiO_2 binary assembly was not controlled, this morphology demonstrates that polymer-coated nanoparticle chains possess sufficient mechanical integrity to maintain their 1-D structure when blended and cast onto surfaces.

In conclusion, the synthesis of ferromagnetic cobalt nanoparticles using well-defined polymeric surfactants is described. By control of surfactant structure, ferromagnetic colloids possessing a polymeric shell were synthesized. These functional colloids are intriguing building blocks for bottom-up materials synthesis and novel mesoscopic assemblies.

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Supporting Information Available: Detailed experimental procedures on the preparation of polymers and nanoparticles and additional TEM, AFM/MFM, XPS, XRD, and VSM data. This material is available free of charge via the Internet at http://pubs.acs.org.

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