Self-assembly and magnetic properties of cobalt nanoparticles

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Two- and three-dimensional superlattices of passivated cobalt nanoparticles were formed by a self-assembly technique. The size and stabilization of the cobalt nanoparticles are controlled by using the combination of oleic acid and triphenylphosphine. The cobalt nanoparticles are stable for at least 90 days without oxidation at room temperature under ambient conditions. The magnetic properties of the cobalt nanoparticles in different forms are compared, which provides helpful information on the magnetostatic interaction of the nanoparticles. © 2003 American Institute of Physics. [DOI: 10.1063/1.1586481]

Nanoparticles (NPs) of the size less than 10 nm are particularly interesting because the particle size is smaller than the dimension of atomic or ionic diffusion length, electronic elastic and inelastic mean free path length, and the magnetic domain size. 1-5 Many new phenomena and properties are expected to appear in the NPs systems. The size and shape specificity of nanoparticles naturally serve as building blocks expected to appear in the NPs systems. The size and shape of the self-assembled passivated NP superlattices (SLs) or NP arrays. 6 In this emerging field, monodisperse magnetic NPs are desirable owing to their broad range of applications, such as data storage devices and sensors. 7-10 The advances in preparing semiconductor and metallic NPs, specifically by the method of injecting molecular precursors into hot organic surfactant solution, have improved the NP samples remarkably, with good size control, narrow size distribution, and good crystallinity of individual and disperse nanoparticles. 11,12

In this letter, we report our experiment on the synthesis of cobalt NPs using thermal decomposition of octacarboxylidicobalt. 13 This method provides a “clean” route for the preparation of the material since the cobalt is the only nonvolatile product of the reaction: [Co2(CO)8]→2Co+8CO. 14,15 We employed a combination of surfactants in the presence of stabilizing ligands triphenylphosphine and oleic acid in controlling the particle growth, stabilizing the particles, and in preventing the oxidation. The purpose of using the triphenylphosphine, instead of the tributylphosphine or trioctylphosphine, is that the phenyl can provide greater steric hindrance than that of the straight chain alkyl. It can be controlled to synthesize cobalt NPs with small size. In addition, the price is cheaper and size dispersion of the cobalt NPs can be further narrowed through size-selective precipitation. 16 Two-dimensional (2D) and three-dimensional (3D) SL structures were examined using transmission electron microscopy (TEM). Low-resolution and high-resolution TEM images were obtained using JEOL-200CX operating at 120 kV and Philips CM200-FEG operating at 200 kV. A Philips CM200-FEG transmission electron microscope equipped with cooling sample stage and Gatan imaging filter system was employed to analyze the component of cobalt NPs. The structure of the nanoparticles was examined using Rigaku D/MAX 2400 x-ray diffractometer with Cu Kα radiation (λ=1.5406 Å). Magnetic measurement was conducted in a MPMS-5 superconducting quantum interference device (SQUID) magnetometry.

It is generally accepted that a temporal separation of the nucleation and the growth stages is required for the production of a monodisperse colloid. 17 The dichlorobenzene solution of Co2(CO)8 was injected into hot reactant (~220 °C) to form a large number of critical nuclei. The growth of the nuclei continues by adding cobalt containing species to the surface of the particles with a decreasing reaction rate (temperature tuned to 185 °C). This process can narrow the size distribution in diameter of the cobalt NPs. The colloid is stable when a repulsive force of sufficient strength and range exists to counteract the combined attractive forces. The cobalt NPs experience strong Van der Waals attractions and magnetic dipole interactions, which is a great challenge to stabilize these systems. The combination of triphenylphosphine and oleic acid produces a tight ligand shell on the surface of Co NPs, which allows the particles to grow steadily while protecting them from aggregation and oxidation. In order to identify if there is oxygen in the cobalt NPs, electron energy-loss spectroscopy (EELS) is used to analyze the components of the superlattices of the cobalt NPs. As shown in Fig. 1, the strong Co L2,3 edge is at 779 and 794 eV. The O K-edge signal (532 eV) does not appear, indicating the component of the SL is pure cobalt.

Slow evaporation of a heptane dispersion of cobalt NPs spread on a flat substrate leads to well-organized SL structures. When the solution concentration is nearly 1%, the monodisperse cobalt NPs with a 7-nm average diameter are self-assembled into large area of well-defined 2D SLs as shown in Fig. 2(a). High concentration at the initial stage and
octane dispersion of the cobalt NPs evaporated at high temperature, for example, 40 °C, leads to a 3D self-assembly structure. Figure 2(b) shows the TEM image of the 3D SL of ~5-nm cobalt NPs. The ordered area in the 3D SLs extends over 0.6 μm × 0.6 μm, as is shown in Fig. 2(b). The 2D and 3D SLs of the cobalt NPs are hexagonal stacking structures, and the particles in the second layer occupy the sites of the hexagonal arrangements. They are usually separated by domain boundaries resulting from the solvent evaporation rate, the rough surface morphology, and the defects on the surface of the substrate.18

The evaporation rate of organic solvent is critical in the self-assembly of cobalt NPs. A slow evaporation rate does not form well-organized SLs. The carrier solvent with high boiling point for the cobalt NPs allows slow evaporation at high temperature. High thermal energy permits the particles to diffuse to their lowest energy SL site during evaporation, providing well-defined 3D SLs.

X-ray diffraction (XRD) of the 3-nm C_{18}H_{33}O_{2}/C_{18}H_{15}P passivated Co NPs prior to the annealing shows a large broad structure. Figure 2(b) shows the TEM image of the 3D SL of ~5-nm cobalt NPs. The ordered area in the 3D SLs extends over 0.6 μm × 0.6 μm, as is shown in Fig. 2(b). The 2D and 3D SLs of the cobalt NPs are hexagonal stacking structures, and the particles in the second layer occupy the sites of the hexagonal arrangements. They are usually separated by domain boundaries resulting from the solvent evaporation rate, the rough surface morphology, and the defects on the surface of the substrate.18

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X-ray diffraction (XRD) of the 3-nm C_{18}H_{33}O_{2}/C_{18}H_{15}P passivated Co NPs prior to the annealing shows a large broad peak centered at θ=42.4°, as shown in Fig. 3(a). As the particle size increases, for example, to 7 nm, the XRD pattern shown in Fig. 3(b) indexes to a crystalline structure known as the metastable ε-cobalt for cobalt at ambient pressure, which is similar to that of the β-manganese (a high-temperature phase of manganese). Its unit cell contains 20 cobalt atoms, which do not pack into an ideal close-packed structure of the bulk fcc and hcp cobalt.19 Annealing a similar sample to 500 °C under Ar+H₂(5%) for 3 h, completely transforms the structure to the fcc phase [Fig. 3(c)]. Subsequent cooling does not return the sample to its original ε-cobalt structure, which is in good agreement with the structure of the cobalt NPs obtained elsewhere.20 It is found that an amount of cobalt oxide (CoO) can be formed during the annealing process. The sharp peak observed is due to the sintering and annealing of the crystal.

Magnetic properties of the ~7-nm cobalt nanoparticles deposited on highly oriented pyrolytic graphite (HOPG) substrate are measured by SQUID using a standard airless procedure. The magnetization as a function of the temperature in a 10-Oe field between 5 and 300 K determines the blocking temperature using a zero-field cooling procedure. Figure 4(a) show the typical result for magnetic NPs, below the critical size at which particle becomes a single domain magnet and is small enough to display superparamagnetism.21 From the concrete measurement data, the blocking temperature (T_b) is 92 K. The broad transition from superparamagnetism to ferromagnetism shown in Fig. 4(a) around ~92 K is probably due to the magnetostatic particle interactions in the close-packed arrays. The blocking temperature should roughly satisfy the relationship

\[ T_b = KV/30k_B \]

where K is the anisotropy constant, k_B Boltzmann’s constant, and V is the average volume of the particle. With the knowledge of the blocking temperature and the particle size, the anisotropy constant is 2.1×10^4 erg/cm^3 for the Co particles, which is smaller than that of the bulk fcc cobalt (2.7×10^6 erg/cm^3).

Figures 4(b) and 4(c) show the hysteresis loop of the cobalt NPs powder compacted into a capsule made from bone powder at 250 and 10 K, respectively. Cobalt NPs show no hysteresis in their magnetization data at 250 K, indicating a superparamagnetism behavior at room temperature. Below the blocking temperature, the cobalt NPs are ferromagnetic. At 10 K, the remanent magnetization \( M_r \) is about 1.5 emu/g; the coercitive field \( H_c \) is 163 Oe, and the magnetization at saturation \( M_s \) is estimated to be only 14.0 emu/g (the esti...
mation is based on an extrapolation of curves of $H/M$ versus $H$. Figure (d) shows the hysteresis loop of diluting particles with wax (a mass ratio of cobalt nanoparticles: wax = 1:4). There is a clear change in the shape of the hysteresis loop. The $M_r$ reaches 7.3 emu/g, $M_s$ reaches to 59.6 emu/g, and $H_c$ increases from 163 to 600 Oe in comparison with the isolated cobalt nanoparticles powder. Figure (e) shows the hysteresis loop of ordered arrays of cobalt nanoparticles on HOPG substrate. The $M_r$ reaches 12.6 emu/g and $H_c$ increases to 790 Oe. But the improvement of $M_s$ is not obvious in comparison to the diluting particles with wax, at 61.6 emu/g. These values (Table I) are low compared to those obtained for the bulk phase. The observed changes cannot be attributed to the coalescence of the cobalt NPs. Since TEM images taken over large areas of the sample show no evidence of the coalescence. Among the possible explanations for the change in magnetic properties is the exchange coupling between adjacent particles. The dipole coupling enhancements are attributed to the long-range order of the 2D lattice and collective “flips” of the magnetic dipoles.

In conclusion, the improved high-temperature thermal decomposition synthesis routes to monodisperse cobalt NPs have been presented. Controlled growth and steric stabiliza-

![Table I. Magnetic properties of cobalt NPs under different physical states.](image)

<table>
<thead>
<tr>
<th>Physical state</th>
<th>$M_r$ (emu/g)</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r/M_s$</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder into a capsule</td>
<td>14.0</td>
<td>1.5</td>
<td>0.11</td>
<td>163</td>
</tr>
<tr>
<td>Diluting particles with wax</td>
<td>59.6</td>
<td>7.3</td>
<td>0.12</td>
<td>600</td>
</tr>
<tr>
<td>On HOPG substrate</td>
<td>61.6</td>
<td>12.6</td>
<td>0.20</td>
<td>790</td>
</tr>
</tbody>
</table>

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13. A three-neck flask with 40 ml of dichlorobenzene is heated to ~220°C under N2 and stirred for a certain time to exclude ambient air, and then 2.0 mmol of oleic acid and 2.0 mmol of triphenylphosphine are added. In a separate reaction vessel, 2 mmol of CO2(CO)10 is combined with 5 ml of dry dichlorobenzene, warmed briefly to nearly 60°C under N2 until fully dissolved, and finally rapidly injected into the flask. The solution turns black and quickly foams as CO2(CO)10 decomposes, nucleating Co NPs and releasing CO gas. After the CO gas disappears, the black solution is refluxed at 185°C for 20 min. Then the black solution is cooled to room temperature. Particles are precipitated by adding ethanol to the dispersion.