Synthesis and Characterization of Large Colloidal Cobalt Particles

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Large colloidal environmentally stable silica-coated cobalt particles were synthesized by combining the sodium borohydride reduction in aqueous solution and the Stöber method. Low size polydisperse cobalt spheres with an average size of 95 nm were synthesized by using a borohydride reduction method and were subsequently coated with a thin layer of silica by means of hydrolysis and condensation of tetraethylorthosilicate (TEOS) in an aqueous/ethanolic solution. The large uniform cobalt spheres consist of smaller metallic Co clusters, explaining the superparamagnetic behavior of the spheres. The particles were investigated by transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM).

1. Introduction

Magnetic nanoparticles have attracted increasing interest among researchers of various fields because of their promising applications in high-density magnetic recording media, ferrofluids, magnetic refrigeration systems, and biomedicine.1,2 Numerous attempts to synthesize monodisperse magnetic nanoparticles with controllable sizes have been reported.3 The main difficulty for the use of the room-temperature ferromagnetic materials (Fe, Ni, Co, and their alloys) arises from their instability toward oxidation in air, which increases as the size gets smaller. Colloidal stability of small single-domain particles in nonmagnetic carrier fluids is achieved by coating the particle with a material that prevents close approach of the particles, thereby reducing the possibility of aggregation via van der Waals or magnetic attractions.4 In general, suitable coatings (made of either inorganic ceramics or organic polymers) are required to endow the magnetic nanoparticles with great stability against agglomeration and harsh chemical environments.5 The coating of magnetic nanoparticles with silica shells6 provides exceptional advantages such as environmental stability and control of interparticle interactions by controlling the shell thickness. In the presence of an insulating silica shell, the magnetic exchange interaction is avoided, and the magnetic dipolar coupling, which also leads to cooperative magnetization reversals of adjacent particles,7 can be strongly reduced. Additionally, the surface of silica is terminated by silanol groups that can react with various coupling agents to covalently attach specific ligands to the surface of these magnetic particles.

Below a critical particle volume V, which depends on the magnetic anisotropy density K and the magnetization M, individual nanoparticles within a dispersion become single-domain nanomagnets. This behavior can be modeled as a single giant magnetic dipole moment. At low temperatures, this moment is pinned along one of the energetically favorable “easy” (crystalline) axes of the particle,1,2,8 therefore exhibiting ferromagnetic behavior. Above a characteristic temperature (the “blocking temperature”), thermal fluctuations can overcome the anisotropy barrier E0 = KV, so the moments can fluctuate among the different easy directions. The dispersion is then said to be superparamagnetic.9 One should note, however, that the experimentally determined blocking temperature may vary over several 10 K when the time window of the measurement is changed from a few seconds to the nanosecond range.10

In this article, we describe the synthesis of large cobalt particles (95 nm diameter) with a reasonably narrow size distribution (<20%) by reducing cobalt chloride hexahydrate with sodium borohydride in the presence of citric acid in an aqueous medium. These particles are subsequently protected with a thin outer shell of silica. Owing to their remarkable morphology, these silica-coated cobalt nanoparticles appear to be very interesting materials.
for studying the magnetic interactions among the inner (smaller) clusters within a single (large) sphere, and for studying the interparticle interactions among the larger particles, since the silica shell thickness can be tuned to yield different interaction potentials.

2. Experimental Section

The synthesis of silica-coated cobalt nanoparticles was performed as follows: 0.1 mL (0.4 M, 4 × 10^{-5} mol) of cobalt chloride hexahydrate (Fluka) in H_2O was added to an aqueous solution (100 mL) of NaBH_4 (4.4 mM, 4.4 × 10^{-4} mol) (Riedel de Haen) and citric acid monohydrate (Riedel de Haen) (2 × 10^{-6} M, 2 × 10^{-7} mol) under mechanical stirring. Immediately following the cobalt reduction, 400 mL of an ethanolic solution containing 15 mL of tetraethoxysilane (TEOS) (Aldrich 98%) was added. After 15 min, the solution was centrifuged, and the precipitate was redispersed in ethanol (40 mL).

Transmission electron microscopy (TEM) measurements were performed on a F20 Tecnai microscope operating at 200 kV. Samples for TEM were prepared by depositing them on a standard amorphous carbon-coated copper grid. Magnetic measurements were performed on a Quantum Design vibrating sample magnetometer (VSM).

3. Results and Discussion

Particle Synthesis. Cobalt ions were reduced to metallic cobalt by sodium borohydride (NaBH_4), according to the following reactions,^11,12

\[
2\text{CoCl}_2 + 4\text{NaBH}_4 + 9\text{H}_2\text{O} \rightarrow \\
\text{Co}_2\text{B} + 4\text{NaCl} + 12.5\text{H}_2\text{O} + 3\text{B(OH)}_2 \\
4\text{Co}_2\text{B} + 3\text{O}_2 \rightarrow 8\text{Co} + 2\text{B}_2\text{O}_3
\]

If the two reagents are rapidly mixed and the product is handled under argon, the reduction of CoCl_2 (aq) with NaBH_4 yields ultrafine particles of Co_B as the primary product. When exposed to oxygen, a sacrificial reaction takes place whereby boron is oxidized while cobalt is reduced,^13 resulting in the conversion of Co_B to Co(s). In fact, Brown and co-workers^13 previously pointed out the complexity of this chemistry, since the metal ions serve as catalysts for BH_4^- oxidation by water. Pileni and co-workers also reported the synthesis of well-defined and low size distribution cobalt nanocrystals using reverse micelles and sodium borohydride as reducing agents, although they were smaller in size.\(^5e,14\)

A nucleation burst takes place immediately after the addition of the cobalt chloride solution to a previously prepared sodium borohydride and citric acid aqueous solution. In the first step, the nuclei grow to nanosized primary clusters by diffusional capture of remaining atoms. In the second step, depending on the reaction conditions, the primary clusters aggregate, leading to the formation of larger spherical particles accompanied by a narrowing of the size distribution.\(^15\) The results are strongly dependent on the amount of O_2 present in the aqueous solution and on the citrate/Co_2^{2+} molar ratio.\(^6b\) Furthermore, to stimulate nucleation, the cobalt chloride solution has to be added quickly and with good stirring to a freshly prepared sodium borohydride solution, so that the immediate reduction of cobalt ions takes place. The results are strongly dependent on the age of the solutions, so using freshly prepared solutions was necessary to obtain reproducible results. Citrate ions present in solution are believed to prevent further growth through double-layer repulsion between negatively charged cobalt nanoparticles.\(^6c\) However, this stabilization cannot avoid the aggregation of clusters to form bigger particles. The effect of citrate ions on the reaction was not studied in detail.

Figure 1 shows a TEM image and size histogram of the spherical cobalt particles synthesized by reducing cobalt chloride hexahydrate in water solution and further coated with silica in an aqueous/ethanolic solution. silica-coated cobalt colloids appear to be fairly spherical and relatively monodisperse. The average diameter of the magnetic particles was about 95 nm. Statistical analyses on the size of the various core—shell particles show that the standard deviation for the diameter of cobalt core is within 19%.

If the cobalt chloride solution is added quickly to the sodium borohydride and citric acid solution, nucleation occurs quickly (“instantaneous” nucleation), resulting in a more monodisperse particle size. If the reactants are added slowly, there will be a continuous generation of nuclei during the mixing. The first nuclei formed will act like seeds and will further grow to larger sizes before aggregation, forming secondary particles.

Particle Morphology. By the procedure described above, spherical cobalt particles with an average diameter of 95 nm were synthesized. These cobalt particles were composed of smaller clusters, as seen in Figure 2. This TEM picture clearly reveals the aggregated nature of the final particles, which consist of smaller subunits (indicated by arrows). Cobalt clusters formed in water solutions are poorly stabilized by citrate ions and tend to coalesce forming larger aggregates. These clusters tend to sinter together into a spherical shape in order to minimize the surface energy. This morphology is different from nanoparticles synthesized by a similar method (yielding smaller and more compact nanoparticles coated with an outer silica shell\(^10\)), owing to the presence of dissolved oxygen.\(^12\) Dissolved oxygen in the aqueous medium favors the formation of metallic cobalt nanoparticles as confirmed by energy-dispersive X-ray (EDX) analysis (Figure 3). However, the EDX analysis does not exclude the possibility of the existence of remaining cobalt boride (Co_B) which is a weak ferromagnet with a Curie temperature, T_C, of

![Figure 1](image-url)
433 K and a magnetic moment per Co atom of ∼0.8 μB. Also, the dia- and soft ferromagnetic cobalt silicides (CoSi, Co2Si, Co3Si, and CoSi2) or cobalt oxide compounds could be partially formed during the synthesis. The strong temperature-dependent change of the saturation magnetization may reflect the presence of these ferromagnetic compounds with a lower Curie temperature than metallic Co, although no unambiguous conclusion can be drawn based on these measurements.

Silica-Coated Cobalt Particles. Once the 95 nm cobalt nanoparticles become thermodynamically stable for several minutes, they can be coated as TEOS hydrolyzes and condenses onto their surface. It can be seen that the cobalt particles are uniformly coated with a silica shell of 10 nm on average (Figures 1 and 2). It is important to note that, despite the lack of a silane coupling agent in the coating process, only composite particles with one core (see Figure 1) were observed in several tests over an area of 3 × 3 mm (TEM grid). No dimers or trimers were found. Furthermore, all the particles contained a magnetic core and no pure silica particles were found. The absence of pure silica particles is consistent with the relatively large ratio of cobalt particle surface per volume compared to the added amount of TEOS.17 The silica, which precipitates from the hydrolysis and condensation of an optimized amount of TEOS in water/ethanol solution is fully exhausted by deposition onto the surface of the cobalt colloids. The silica shell thickness can be therefore controlled by adjusting the initial amount of TEOS yielding large silica-coated cobalt colloids with controlled interparticle distance.

The principal idea for the formation of an outer silica shell described here is to avoid, or at least to slow, the further oxidation of the cobalt cores. This was clearly shown for samples with an outer shell that kept the characteristic gray color for longer times compared to those without this kind of protection.

Magnetic Measurements. The 95 nm particles are above the critical size at which Co particles become a single-domain magnet.18 To investigate the magnetic properties of such well-defined and insulated Co nanoparticles, they were mechanically compacted. If the sample is measured at low temperature, the width of the hysteresis loop yields information on the magnetic anisotropy density and on the potential barrier for magnetization reversal. Figure 4 shows hysteresis curves recorded at 5 and 300 K showing a coercivity of 40 Oe at 5 K. This small value for the coercivity in 95 nm Co particles is indicative of either demagnetization interactions between the clusters or the coexistence of soft (low Curie temperature) ferromagnetic compounds within the particle. Ferromagnetic behavior at room temperature would be expected for a fully magnetized metallic Co sphere with 95 nm diameter.19 The magnetic moments of the clusters forming the nanoparticles are not coupled ferromagnetically, which must be due to atomically thin, antiferromagnetic or diamagnetic layers separating the clusters. This leaves only quite strong dipole–dipole interactions between the clusters, which favor complex noncollinear20 or possibly antiferromagnetic orientations and reduce the overall moment of the particle.21 The magnetization measurements at 5 K also reveal a relatively large paramagnetic contribution, that is, a temperature-dependent large high-field susceptibility. The possible origin of the paramagnetic contribution is the presence of uncompensated spins at the particle interfaces22,23 and the presence of small weakly coupled superparamagnetic Co clusters.24 The open hysteresis loop with a small coercive field of 50 Oe at 5 K is symmetric with respect

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References

to the $y$ and $x$ axes, and typical for a superparamagnetic ensemble measured below its blocking temperature. It cannot be the result of the presence of antiferromagnetic CoO in the 95 nm spheres, which would yield an exchange-shifted hysteresis loop and much larger coercive fields.\textsuperscript{24}

Domain structure and interparticle interaction information can also be derived from zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves. In ZFC (FC) measurements, the sample is cooled in zero (large) magnetic field and then heated in a small field while the net magnetization of the sample is recorded. Figure 5 shows the ZFC–FC magnetization versus temperature curves for the silica-coated cobalt particles. The sample was first cooled at zero magnetic field to 2 K, then a 50 Oe magnetic field was applied, and magnetization measurements were made as a function of increasing temperature. ZFC–FC magnetization curves exhibit the typical blocking process of an assembly of superparamagnetic particles with a wide distribution of blocking temperatures at $T_B \approx 130$ K, where a transition between the “ferromagnetic” blocked state and the superparamagnetic state occurs.\textsuperscript{25}

One can point out that the clusters forming the 95 nm spheres should have an average diameter much smaller than 10 nm or should have a very small magnetic anisotropy energy density on the basis of the low blocking temperature observed in the ZFC–FC curves. Previous reports on magnetically harder, surface-oxidized fcc 11 nm cobalt nanoparticles showed blocking temperatures around 260 K.\textsuperscript{19,23} In our case, the small clusters are mainly metallic, less than 10 nm in size, and coupled, since the irreversibility of the ZFC–FC curves could indicate a magnetic coupling among the small metallic clusters inside the larger spheres.

4. Conclusion

A simple method to synthesize large cobalt colloidal particles with an average 95 nm diameter via controlled aggregation of cobalt clusters is reported. The Co particles are spherical cluster-based aggregates with a low size dispersion ($\lesssim 20\%$), as determined by TEM. The particles were coated with a protective silica layer without using a silane coupling agent isolating the magnetic cores. The magnetic measurements show the superparamagnetic behavior of these large cobalt particles due to demagnetizing interactions between the smaller clusters within the larger 95 nm nanoparticles.

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