Chemical synthesis of low-coercivity, silica/Co composites for high-frequency magnetic components

Himani Sharma*, Markondeya Raj Pulugurtha, Rao Tummala
Packaging Research Center, Georgia Institute of Technology, 813 Ferst Drive, Atlanta GA 30332, USA

HIGHLIGHTS

- Chemical synthesis of <10 nm cobalt nanoparticles with thin silica shell for electronic device application.
- Correlation of structural and magnetic properties.
- Low coercivity of 20 Oe showed exchange-coupled cobalt nanoparticles.
- High-resolution TEM showed thin silica shell of ~4-5 nm.

ARTICLE INFO

Article history:
Received 18 August 2015
Received in revised form 23 January 2016
Accepted 30 January 2016
Available online 9 March 2016

Keywords:
Magnetic materials
Nanostructures
Chemical synthesis
Electron microscopy
Magnetometer
Magnetic properties

ABSTRACT

The paper reports correlation between processing, structural and magnetic properties of cobalt nanoparticles dispersed in an insulating oxide matrix. High-temperature, chemical decomposition approach was utilized to achieve highly-dispersed, ultra-fine cobalt nanoparticles in silica matrix. Synthesis parameters such as precursor to passivating agent ratio were designed to control the metal-to-oxide ratio so as to promote magnetic interactions between the metal particles while keeping the cobalt particle size in sub-nanometer. High-resolution TEM and XRD studies were carried out to demonstrate face-centered phase of single-crystal cobalt particles of size ~8–10 nm monodispersed in thin silica matrix. The particle size variation as a function of precursor to passivating agent ratio was also studied to yield process conditions for ultra-fine nanoparticles. Composites with sub-10 nm metal particles showed superior soft magnetic properties with a lowest coercivity of 10 Oe. The reduction in coercivity with such fine particles is attributed to the transition to superparamagnetic regime. Larger particles showed higher saturation magnetization and higher coercivity of 100 Oe. The coercivity decreased with further increase in particle size from ~50 nm to 80 nm because of the transition from single domain to multi-domain structures.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The technological applications of highly dispersed nanoparticles with superior properties have potential to revolutionize many aspects of modern electronics. The need for miniaturization in portable electronic devices with high efficiency, has led to growing interest in such nanoparticle materials and processes especially for passive electronic components such as capacitors, antennas and inductors [1,2]. In particular, nanomagnetic materials in inductors have gained momentum due to their desirable properties such as high saturation magnetization ($M_s$), low coercivity ($H_c$), and an appropriate anisotropy field ($H_k$) [3]. This combination of magnetic properties enhances the key parameters such as permeability, quality factor, and frequency stability, directly affecting the inductor performance for power and RF components. Traditionally, thick magnetic cores are composed of ferrites that are limited by lower $M_s$ and poor frequency stability because of their low FMR (ferromagnetic resonance) frequency [4,5]. Metal-polymer composites with larger spherical particles show higher losses from eddy-current, lower resistivity and domain wall resonance [6,7]. Nanoparticle composites, on the other hand, show low permeability because of demagnetization. Improved permeability and frequency-stability are achieved by reducing the metal particle size to nano-scale while maintaining close proximity within particles to facilitate exchange coupling. However, such nano-scale inter-particle separation between nano-grains, can only be achieved in sputtered magnetic thin films [3,8,9] that are grown in highly
controlled environment that not only makes them expensive but also difficult to form multilayered thick structure that can handle enough power. Solution-derived, larger scale nanocrystals syntheses have more recently gained interest for their low-cost and tight size control [10], however, most of these superstructures are self-assembled with application in biological, medical and pharmacological fields as biosensors, drug-delivery capsules, catalysts or magnetic data storage [11,12]. The primary reason for limited application of chemically-derived nanoparticles in consumer technologies is the lower product yields [13] that lends insufficient amounts for thick magnetic cores in components such as inductors. In the recent past, a few chemical methods have been devised to produce silica-coated metal nanoparticles at gram scale [14,15], however they showed hard magnetic properties with much larger coercivity rendering them unsuitable for power applications. A key factor to utilize solution-derived magnetic nanoparticles in power passives is to achieve nanocomposites with high metal densities that can be correlated to energy storage densities. This paper investigates the magnetostructural correlation of solution-derived cobalt nanoparticles with high metal densities for their application in power electronics. Synthesis process was tuned to achieve cobalt nanoparticles (<10 nm) with high mono-dispersity in an insulating oxide matrix to yield exchange-coupled metal nanoparticles with superior soft magnetic properties.

2. Experimental

The silica-coated nanoparticles were synthesized using a high-temperature organo-metallic reaction that was pioneered by Hyunjoon Song’s group [15]. This synthesis approach targets to achieve silica shell on a fine cobalt nanoparticle core. A schematic of the methodology is shown in three steps in Fig. 1, illustrating different coating on the nanoparticles at different stages of the synthesis, including the organic and the oxide. The organic shell of oleylamine (OA) serves dual purposes, acting as a solvent as well as a passivating layer that prevents particle agglomeration and Ostwald ripening at higher temperatures. The process begins with thermal decomposition of (cobalt acetylacetonate Co(acac)₂) precursor, to form cobalt oxide seeds that are passivated by the organic ligand, oleylamine (Fig. 1, step-1). The second step involves suspending the OA/CoO nanoparticles in a non-polar organic solvent (cyclohexane) and hydrolyzing silica precursor, tetramethylorthosilicate (TMOS) on the cobalt oxide/OA nanoparticles through a nonionic surfactant-stabilized water-in-oil microemulsion process at room temperature [16].

The hydrolysis of the alkoxide in this base-catalyzed (with NH₄OH) reaction tends to form a three-dimensional network of xerogel, entrapping the chelated cobalt oxide nanoparticles in it (Fig. 1, Step-2). The facile silica hydrolysis on oxide nanoparticles was carried out at room temperature for nearly 60 min, followed by multiple cycles of dispersion and precipitation in ethanol for washing away unreacted TMOS and byproducts of the hydrolysis. The CoO/SiO₂ nanoparticles were finally dried at room temperature to yield stable brown/green powders. The final step (Step-3, Fig. 1) consisted of thermal treatment for reduction of metal oxide to metal, densification of silica, and elimination of organics. It was carried out in a reducing atmosphere of 10% H₂ at 600 °C for various intervals of time to produce optimized fine cobalt nanoparticles with silica shells.

2.1. Material characterization

The nanoparticles were characterized for structural, morphological as well as magnetic properties at all stages. Morphology and the particle size distribution were studied using TEM (JEOL 100CX-II transmission electron microscope, operated at 100 kV). The high resolution images were captured using FEI Tecnai F30 transmission electron microscope (HRTEM) with a TEM resolution limit of 1.7 Å, operated at 200 kV. Sample preparation for all TEM imaging was carried out by suspending nanoparticles in ethanol and dispensing.

![Fig. 1. Schematic illustration of evolution of core/shell nanoparticles; Step-1) Thermal decomposition of cobalt precursor in OA to form OA-coated CoO; Step 2) Room temperature hydrolysis of TMOS on CoO nanoparticles; Step 3) Gas-phase reduction of CoO to Co, removal of organics and silica compaction in at 600 °C for 4 h in 10% H₂.](image-url)
two drops on carbon-coated grids (Ted Pella) and drying them in air. Structural information was obtained by X-ray diffraction (XRD-Philips 1813 diffractometer, Westborough, MA) while the magnetic characterization was performed using B–H loops obtained with a vibration sample magnetometer (VSM, Lakeshore 736 series, Westerville, OH) at room temperature (25°C). For magnetic studies, the samples were prepared as metal-polymer nanocomposites, where the silica-coated cobalt nanoparticles were dispersed in epoxy polymer with volume fraction of above 80%. The composite average particle size increases with capping agent concentration due to increasingly stronger cross-linking interaction between the cobalt (nanoparticle) domains. These interactions influence both the energy and entropy of the cluster formation and lower the free energy of the system, thereby favoring larger cluster (particle) formation.

The particle size variation as a function of precursor to passivating agent ratio is summarized in Fig. 2(e), indicating lowest particle size of CoO is obtained at critical ratio of 1:50.

In addition to the increase in particle size, the OA concentration also played a role in determining the crystallographic phase of CoO nanoparticles. At the precursor-to-ligand ratio of 1:75, CoO particles were hexagonal in shape (shown in Fig. 2(c)) as compared to spherical at all other Co(acac)2:OA ratio. A high resolution TEM image, shown as an inset in Fig. 2(c), clearly shows six edges to the hexagonal pyramidal CoO particle of size ~35 nm. These results are in accordance to literature [18] where it was shown that hexagonal pyramid-shaped nanocrystals are predominant over nanoparticles. At the precursor-to-ligand ratio of 1:75, CoO particles are spherical. Further increase in the OA to 1:75 ratio, tended to increase the particle size to 35 nm and thereby stabilizing the size beyond OA concentration of 1:100 (Fig. 2(e)). It is believed that very high concentration of oleylamine leads to high steric hindrance between the ligands which lead to ineffective chelation of oleylamine with the metal oxide particles leading to particle growth, as seen in case of 1:75 and 1:100. Literature describes the correlation between particle size and capping agent by statistical mechanical model which quantifies the free-energies of nanoscale bonding (or particle aggregation) at different capping agent concentrations [17]. Beyond a critical capping agent concentration, the average particle size increases with capping agent concentration due to increasingly stronger cross-linking interaction between the cobalt (nanoparticle) domains. These interactions influence both the energy and entropy of the cluster formation and lower the free energy of the system, thereby favoring larger cluster (particle) formation.

3. Results and discussion

3.1. Role of Co(acac)2:OA ratio in CoO synthesis

The first part of this study was to optimize the cobalt precursor (cobalt acetylacetonate Co(acac)2) to organic ligand (Oleylamine) ratio, to yield finest metal core in a silica shell. Thermal decomposition of cobalt acetylacetonate (shown in step-1 in Fig. 1) at elevated temperatures of 220 °C for 30–40 min was carried out to form cobalt oxide seeds that were passivated with OA. The particle size of these nucleated cobalt oxides were determined by the Co(acac)2:OA ratio. The ratio was thus changed from very low passivating agent content (1:10) to high content with ratio of 1:100. The morphological effect on the particle size of CoO is shown in Fig. 2 (a–d). As expected, the lower oleylamine concentration at 1:10 yielded much larger CoO particle size of ~80 nm. The particle growth is attributed to Ostwald ripening at a higher reaction temperature of 220 °C when the finer particles fuse with larger ones due to low OA concentration. As the oleylamine concentration is increased, tighter control on the particle size is achieved with increased metal-ligand chelation that prevents particle fusion. Increasing the Co(acac)2:OA to 1:25 and then to 1:50 had shown continuous drop in CoO particle size to 30 nm for 1:25 and 15 nm for 1:50. However, further increase in the OA to 1:75 ratio, tended to increase the particle size to 35 nm and thereby stabilizing the size beyond OA concentration of 1:100 (Fig. 2(e)). It is believed that very high concentration of oleylamine leads to high steric hindrance between the ligands which lead to ineffective chelation of Co2+ ions were octahedrally coordinated by the oxygen lattice (JCPDS No. 48-1719; space group, Fm3m) with peaks assigned to (111), (200), and (220) lattice plane. The ratio of 1:75 on the other hand, clearly showed diffraction peaks corresponding to nanocrystalline hexagonal hcp phase of CoO characterized by their signature three peaks (100), (002), (101) at 2θ of 30°–40°. The crystallite size was also calculated with XRD using Scherrer’s formula.

Fig. 2. TEM micrographs of CoO nanoparticles with different precursor to ligand ratio (a) 1:10; (b) 1:50; (c) 1:75 and (d) 1:100; (e) Effect of particle size as a function of Co(acac)2:OA ratio.
formula and was found to be in good agreement with the TEM data (Table 1). A lowest particle size of ~15 nm (TEM) was obtained for a ratio of 1:50 with spherical particles while the crystallite size for the same ratio was calculated to be 7 nm from the broad peaks seen in XRD spectrum (Fig. 3(b)). The higher noise level observed in spectra corresponding to ratio 1:100 can be attributed to thick amorphous passivation layer of oleylamine that scatters the x-rays causing the increase in noise level as seen in Fig. 3(d). The results obtained from XRD and TEM imaging for particle size and crystallographic phases are tabulated in Table 1, suggesting the optimized cobalt precursor to oleylamine ratio of 1:50 to yield finest cubic CoO nanoparticles.

3.2. Optimizing the silica thickness for softer magnetic properties

The core–shell cobalt/silica (Co/SiO₂) structure was obtained by reducing the cobalt oxide in hydrogen atmosphere at 600 °C for 3–4 h. A thin silica shell not only prevents particle sintering and growth during thermal reduction but also provides the much needed electrical insulation between the particles that thereby reduces the eddy currents in the final device. Thus, the thickness of silica shell depends on the CoO to silica precursor (TMOS) ratio and plays a critical role in determining the magnetic properties of the final product. Several ratios were studied to understand the metal oxide dispersion in the silica matrix and yield the thinnest and stable silica coat on the metal nanoparticles. The results of two ratios are presented here, Ratio 1: 0.05 M CoO in cyclohexane with 1 ml TMOS; Ratio 2: 0.15 M CoO in cyclohexane with 1 ml TMOS.

On using a low ratio of CoO:TMOS (Ratio 1), a fluffy network of silica that embeds extra-fine cobalt metal particles (4–5 nm) is obtained, as shown in Fig. 4(a, b). Literature reports that as high as 42% reduction in metal volume can be achieved during thermal reduction of CoO to fcc Co [15,21] due to oxygen elimination at higher temperature. Although these individual fine cobalt nanoparticles possess superior magnetic properties due to their shape and size, their applications are limited since the interparticle

<table>
<thead>
<tr>
<th>Co/OA ratio</th>
<th>XRD phase</th>
<th>Crystallite size (XRD)</th>
<th>Morphology (TEM)</th>
<th>Particle size (nm) (TEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>fcc</td>
<td>60 nm</td>
<td>Spherical and agglomerated</td>
<td>60–80</td>
</tr>
<tr>
<td>1:50</td>
<td>fcc</td>
<td>7 nm</td>
<td>Spherical and dispersed</td>
<td>15–20</td>
</tr>
<tr>
<td>1:75</td>
<td>hcp</td>
<td>30 nm</td>
<td>Hexagonal and dispersed</td>
<td>30–40</td>
</tr>
<tr>
<td>1:100</td>
<td>fcc</td>
<td>20 nm</td>
<td>Spherical and dispersed</td>
<td>25–35</td>
</tr>
</tbody>
</table>
distance prevents any magnetic coupling between them and also lowers the effective cobalt volume fraction. The high level of monodispersity of the cobalt nanoparticle is attributed to the higher silica concentration that formed a porous but thicker (~30 nm) silica matrix during hydrolysis.

XRD of the reduced silica-coated cobalt nanoparticles was also carried out, revealing the cubic phased metallic cobalt nanoparticle, with assigned peaks to (111) and (200) plane of fcc-cobalt (JCPDS No. 15-0806) [15]. The calculated crystallite size of ~8 nm was also in agreement with the TEM images (Fig. 4). The high noise level in the XRD spectrum (Fig. 5) can be attributed to the large amount of amorphous silica matrix that dispersed the x-ray during data acquisition.

An optimized ratio of TMOS:CoO (Ratio 2, 0.15 M CoO in cyclo-hexane with 1 ml TMOS) was later employed to coat CoO nanoparticles with thinner yet stable silica shell, shown in Fig. 6. HRTEM micrographs showed cobalt cores mostly present as single crystals of diameter ~8–10 nm. The particles were monodispersed with narrow size distribution in amorphous silica matrix with inter-particle distance of 3–5 nm. Fig. 7(a) shows cluster of monodispersed cobalt nanoparticles that were mapped for elemental distribution. Based on elemental mapping of cobalt (Fig. 7(b)), the diameter of the cobalt spheres was estimated to be 10 nm, while the thickness of the silica shell, whose signatures are obtained from Si and O mapping (Fig. 7 (c&d), respectively) was much larger. Assuming a uniform silica coating on cobalt core, the thickness of silica around the core, is calculated to be ~ 5 nm.

3.3. Magnetic properties of Co/SiO₂ nanoparticles

The static magnetic properties were studied with magnetization curves measured using vibration sample magnetometry (VSM) at room temperature and correlated to nanostructures. The Co/SiO₂ nanoparticles were mixed with polymer to form composites such that the metal-silica to polymer volume ratio was maintained at 0.80:0.20 for all samples. In addition, for better comparison, all samples were pressed so as to maintain same density of ~3 g/cc. Fig. 8(A) shows a hysteresis loop of cobalt nanoparticles with varied particle sizes. As expected, with the increase in cobalt nanoparticle size, saturation magnetization (Ms) was seen to increase from 15emu/g for < 10 nm cobalt to 100emu/g for the largest particle in this study (100 nm). The increase in Ms is attributed to the increase in the effective metal core volume fraction, compared to oxide shell, with larger particle size. The coercivity, in addition to Ms, also showed strong dependence on particle size (Fig. 9). The magnetic data of cobalt nanoparticles with varied sizes is summarized in Table 2.

For the smallest particle size (<10 nm), a very low coercivity of 20 Oe (Fig. 8(A), curve a) is achieved, indicative of exchange coupling between the particles. To the best of the author’s knowledge, such low coercivity has not been previously observed in solid-state and solution-derived metal nanoparticles. Furthermore, as the particle size is increased (~15–30 nm), the coercivity increased as seen in curve b and c of Fig. 8(A). However, further increase in particle size to 100 nm (curve d, Fig. 8(A)) leads to decrease in coercivity. This grain-size dependence of coercivity is explained through Fig. 9 which follows the classical bell-shaped curve which is well-understood from the literature [22, 24, 29].

With large particles of above 100 nm, multiple domains form within the particle. The number of domains within the particle is dependent on the magnitudes of magnetocrystalline energy, exchange energy and saturation magnetization. The coercivity is low in this case because the magnetization within each domain can be aligned to the other domain by easily rotating the domain wall with lower energy. With reduction in particle size to below 50 nm, the number of domains within the particle reduces to less than 5 [23]. The effective field anisotropy is enhanced in nanoparticles because of dominating magnetocrystalline anisotropy with finer and fewer domains. The dominating surface area further increases the coercivity because of the surface anisotropy and ferromagnetic/antiferromagnetic coupling at the Co/CoO interface [24, 25].
The surface anisotropy \( K \) can be estimated by assuming magnetic anisotropy \( H_k \) to be of the form:

\[
H_k = H_{\text{bulk}} + \frac{H_{\text{surface}}}{D}
\]

(1)

\[
K = K_{\text{bulk}} + \frac{K_{\text{surface}}}{D}
\]

(2)

Where, \( D \) is the metal particle size.

Based on expressions (1) and (2) with finer particles the effective anisotropy increases because of enhanced surface area. The highest coercivity is obtained when the particles transition from multiple domains to a single domain, also known as Stoner-Wohlfarth domains [26]. In these dimensions, the particle cannot accommodate even a single domain wall. Coercivity of magnetic particles is dependent on several factors (1) magnetic anisotropy which can originate from magnetocrystalline or shape anisotropy; and (2) demagnetization factor, which depend on the shape and aspect ratio of the particles, (3) magnetic anisotropy averaging from multiple domains within the particle, (4) Thermal effects.

The coercivity rapidly reduces with size below a critical value because of thermal effects and also from increased exchange coupling between the particles which reduces the effective field anisotropy based on Herzer’s theory [28]. The thermal effects can cause easy reversal of magnetization in this so-called super-paramagnetic limit. The magnetic properties of finer nanoparticles depend strongly on the interplay of energies between local magnetic anisotropy and ferromagnetic exchange which are in turn governed by ferromagnetic exchange length, \( L_{\text{ex}} \) [27]. Due to exchange coupling, the field effective anisotropy constant \( K_{\text{eff}} \) reduces as \( 1/\sqrt{N} \) due to averaging, where \( N \) is the number of exchange

---

**Fig. 6.** HRTEM of silica coated cobalt nanoparticles with ~10 nm metal core and ~5–8 nm silica shell.

**Fig. 7.** Nanoscale elemental mapping of (a) silica coated Co nanoparticle in STEM mode; (b) mapped cobalt (10 nm); (c, d) mapped Si and O (20 nm) overlaying the Co metal core.
coupled grains within the volume of \((L_{ex})^3\) with grain size. However, exchange coupling is presumably absent at these interparticle dimensions, which inhibits further suppression in coercivity.

### 4. Conclusions

Silica-coated cobalt nanoparticles were synthesized using a high-temperature organometallic process to yield highly monodispersed nanoparticles with narrow particle size distribution. The effect of metal precursor to capping agent ratio on particle size and morphology of cobalt nanoparticles was studied using high-resolution TEM and XRD. Hexagonal and face-centered cubic phases of CoO were observed with varying Co(acac)₂:OA ratio. An optimized ratio of 1:50 yielded smallest cubic, particle size of <10 nm. High-density, monodispersed and spherical cobalt nanoparticles (10 nm) were embedded in thin silica matrix to facilitate exchange coupling between the magnetic particles.

Magnetic properties were correlated to the structure, size and distribution of the nanoparticles. The composite with sub-10 nm nanoparticles in superparamagnetic regime showed superior soft magnetic properties with as low coercivity as 20 Oe. With increase in the single-domain particle size, a more coercive nanocomposite was formed due to dominating ferromagnetic anisotropy, increasing the field for reversal magnetization. Beyond the critical particle size (40–50 nm) multi-domain structures are formed within the particle, leading to lowering of coercivity.

### References


