Structure and magnetic properties of SiO$_2$-coated Co nanoparticles

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SiO$_2$-coated Co nanoparticles in a size range of 10 to 50 nm were synthesized by a wet chemical approach, and their structure and magnetic properties were investigated using x-ray diffraction, high-resolution transmission electron microscopy, and a superconducting quantum interference device magnetometer. The structure of the synthesized nanoparticles varied with calcination temperature. When the calcination temperature was as high as 900 °C, the nanoparticles had a core/shell structure: the core was fcc Co and the shell was amorphous SiO$_2$. When the calcination temperature was 800 °C or below, the nanoparticles had a nano-onion structure: the shells from the exterior to the interior were amorphous SiO$_2$, fcc Co, and CoO, and the innermost core was Co$_3$O$_4$. The SiO$_2$ shell had the ability of hindering Co from particle growth during the synthesis procedure and protecting Co against oxidation after the synthesis procedure. The nanoparticles were ferromagnetic. At both low and room temperatures, the saturation magnetization increased with increasing calcination temperature, while the coercivity decreased with increasing calcination temperature. For the nanoparticles calcined at 800 °C or below, the low temperature coercivity was found to be notably higher than the room temperature one due to Co/CoO exchange coupling. For the nanoparticles calcined at 900 °C, the coercivity was relatively low and the saturation magnetization reached the expected values. © 2002 American Institute of Physics. [DOI: 10.1063/1.1483393]

I. INTRODUCTION

Magnetic nanoparticles can be widely used in catalysts, ferrofluids, clinical drug delivery, magnetic storage media, soft magnetic materials, microwave magnetic devices, and electromagnetic wave absorbing materials. In most of those applications, however, the nanoparticles need to be coated with a protective layer prior to being used. For example, in clinical applications the nanoparticles should be protected from leaching in an acidic environment; in high-frequency applications the nanoparticles should be coated with an insulating shell prior to consolidation to achieve high resistivity (low eddy-current loss).

There has been a considerable amount of research involving the preparation, structure, and properties of magnetic Co nanoparticles in the past decade. However, most of this work focused on Co nanoparticles without any protective coating; only a few were devoted to Co nanoparticles coated with protective shells. Recently we have successfully engineered a wet chemical approach to fabricate Co/SiO$_2$ nanocomposite materials, where individual Co nanoparticles were coated with a thin layer of amorphous SiO$_2$. The detailed synthesis procedure was presented elsewhere. Here we present the structure and magnetic properties of the SiO$_2$-coated Co nanoparticles.

II. EXPERIMENTAL PROCEDURE

SiO$_2$-coated Co nanoparticles were synthesized by a wet chemical approach. The main procedures included: (1) preparing the starting precursors containing cobalt and silicon, (2) atomizing the precursors to make colloidal solutions, (3) annealing the solutions to form a precomposite complex, and (4) low temperature calcination to form SiO$_2$-coated Co nanoparticles. The Co concentration in the synthesized nanoparticles was found to be dependent mainly on the precursor concentration and the calcination temperature. In this paper, the nanoparticle samples were prepared using the same precursor but different calcination temperatures of 600, 700, 800, and 900 °C. The volume fraction of Co in these samples was targeted at 50%.

The structure of the nanoparticles was determined by powder x-ray diffraction (XRD) using Cu$K_{\alpha1}$ radiation. Morphology was analyzed using high-resolution transmission electron microscopy (HRTEM). Magnetic properties were studied using a Quantum Design superconducting quantum interference magnetometer.

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III. RESULTS AND DISCUSSION

The HRTEM studies revealed that the synthesized nanoparticles had a core/shell structure: the core was fcc Co and the shell was SiO2; the size of the Co core ranged from 10 to 50 nm. The XRD patterns of four nanoparticle samples synthesized at different calcination temperatures are shown in Fig. 1. As can be seen, all of the diffraction patterns of four samples match only the fcc Co structure and show no peaks for hcp Co. Bulk Co has a hcp structure at room temperature and undergoes a martensitic phase transition to a fcc structure at about 410 °C.21 Different from bulk Co, the Co core in as-synthesized nanoparticles had a pure fcc structure at room temperature. This is believed to be due to the lower surface energy of nanoscale particles.12 Also, there are no detectable Co-oxide peaks in these diffraction patterns. This indicates that the synthesized nanoparticles are free from surface oxidation, due to the protective SiO2 shell. However, we could not determine from these diffraction patterns whether the nanoparticles have an inner Co-oxide core, since the Co atom has a high x-ray absorption coefficient. Figure 1 also shows the XRD pattern of Co3O4/SiO2 nanoparticles, which were formed during the annealing stage of our synthesis procedure and then were converted to the Co/SiO2 nanoparticles during the calcination stage, where the diffraction pattern matches only Co3O4 structure, and there was no evidence of Co, CoO, or Co2O3 peaks. It also should be noted here that no evidence for crystalline SiO2 was detected either in the XRD patterns or in the electron diffraction patterns. As a result, we concluded that the SiO2 phase in the Co/SiO2 nanoparticles is in an amorphous state.

From the (111) diffraction peak, the average size of the inner Co core in the synthesized Co/SiO2 nanoparticles was estimated by the Scherrer formula.22 The estimated results are given in Fig. 2. From the (311) diffraction peak, the average size of the Co3O4 nanoparticles was also estimated to be approximately 25.5 nm. When the calcination temperature was 800 °C or below (see Fig. 2), the Co particle size was close to Co3O4 particle size and increased only slightly with temperature; when the calcination temperature was as high as 900 °C, the Co particle size increased significantly. This indicates that when the calcination was conducted at 800 °C or below, the SiO2 coating remained as an unbroken shell and prevented the coarsening of the Co nanoparticles; at 900 °C, however, the SiO2 coating no longer acted as a barrier to effectively prevent abnormal Co particle growth.

Based on the above HRTEM and XRD results, the structure of the synthesized nanoparticles can be illustrated by Fig. 3(a). However, if the Co3O4 phase has not been completely converted to metallic Co during the calcination stage, the nanoparticles might be of an onion structure as illustrated in Fig. 3(b), where the inner core is Co3O4. Moreover, considering the conversion procedure of Co3+→Co2+→Co, the nanoparticles are more likely of the structure illustrated in Fig. 3(c), where the inner Co3O4 core has a CoO coating.

Both CoO and Co3O4 are antiferromagnetic, with Neel temperatures of TN=270 K23 and TN=33 K,24 respectively. It is well known that, when Co/CoO or Co/Co3O4 system are cooled through TN in the presence of an external field, the CoO or Co3O4 antiferromagnetism gets “turned on” at TN in the presence of the magnetized Co and the magnetic moments in the CoO or Co3O4 choose an axis of magnetization that minimizes their energy of interaction with the Co moment across the interfaces.23,25 As a result, for T<TN, the Co magnetization is biased to the direction of the magnetic moments in the CoO or Co3O4 phase. As long as the memory of that direction is not erased by heating above TN, the Co phase retains a preference for magnetization in that direction. A stronger negative field is required to demagnetize the system than if it had been cooled in zero field. As a consequence, the M–H loop of the Co/CoO or Co/Co3O4 system will be displaced along the field axis if the system is cooled in an external field. Meiklejohn and Bean referred to this field-displaced loop as exhibiting exchange anisotropy, and it was said to result from an exchange coupling between the moments in the ferromagnetic phase and those in antiferromagnetic phase.23 In the following discussion, the field-displaced M–H loop observation will be used to identify the structures illustrated in Fig. 3.

Figure 4 shows the M–H loops of four nanoparticle samples measured at 10 K after they were cooled (from 350

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**FIG. 1.** X-ray diffraction patterns of Co/SiO2 nanoparticles calcined at 600, 700, 800, and 900 °C, and Co3O4/SiO2 nanoparticles.

**FIG. 2.** Average size of Co particles versus calcination temperature.

**FIG. 3.** Structure illustration of SiO2-coated Co nanoparticles.
K) in a magnetic field of 5.5 T. As shown in Fig. 4, the loop for the nanoparticles calcined at 900 °C is symmetrical about zero field, and the exchange bias field $H_{ex}$ is just about 3.9 Oe, which is quite smaller than the coercivity field. This indicates that no or negligible CoO or Co$_3$O$_4$ exists in the 900 °C calcined nanoparticles. That is to say, the surface of the Co is free from oxidation, and the inner Co-oxide core has been completely converted to metallic Co. Thus the engineered wet chemical approach can be used to synthesize Co nanoparticles without containing Co-oxide. However, loop displacements are observed for other three samples. This indicates that those three samples have an onion structure as illustrated in Fig. 3(a) or 3(c). Table I gives the exchange bias fields and coercivity fields of four samples, which were determined from the loops in Fig. 4. As shown in Table I, both $H_{ex}$ and $H_{ex}/2H_c$ decreased with increasing calcination temperature. This is because the size of the inner Co-oxide core decreases with increasing calcination temperature and the diminishing Co-oxide core leads to a subsiding ferromagnetic/antiferromagnetic interface.

Considering that the exchange bias field disappears when the temperature is higher than the Neel temperature of the antiferromagnetic phase, we can distinguish CoO from Co$_3$O$_4$ by measuring the M–H loops at various temperatures. Figure 5 shows the M–H loops of the 600 °C calcined nanoparticles measured at 10, 100, and 300 K after cooling from 350 K in a magnetic field of 5.5 T. In Fig. 5, the notable displacements are observed for the loops measured at 10 and 100 K, while the loop measured at 300 K is symmetrical about zero field. These results reveal that the loop displacements in Figs. 4 and 5 result from Co/CoO exchange coupling, rather than Co/Co$_3$O$_4$ exchange coupling. Thus it can be seen that the nanoparticles calcined at 600, 700, and 800 °C had an onion structure as illustrated in Fig. 3(c).

A typical temperature dependence of zero-field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) for 600 °C calcined nanoparticles is shown in Fig. 6. In order to obtain these results, the nanoparticle sample was cooled in zero field from room temperature to 15 K. Then, a magnetic field of 100 Oe was applied and the ZFCM was measured with increasing temperatures from 15 to 350 K, after which the FCM was measured in the same applied field with decreasing temperatures from 350 to 15 K. Figure 6 shows irreversible magnetization-temperature behavior and no superparamagnetic relaxation behavior. This indicates that the 600 °C calcined nanoparticles are in the ferromagnetic state. The ZFCM and FCM experiments for other three nanoparticles generated the same results. That is to say, four nanoparticle samples all exhibited ferromagnetic behaviors.

### Table I. Exchange bias fields and coercivity fields of SiO$_2$-coated Co nanoparticles measured after cooling from 350 to 10 K in a magnetic field of 5.5 T.

<table>
<thead>
<tr>
<th>Nanoparticle samples</th>
<th>Exchange bias field</th>
<th>Coercivity fields</th>
<th>$H_{ex}/2H_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_{ex}$ (Oe)</td>
<td>$2H_c$ (Oe)</td>
<td></td>
</tr>
<tr>
<td>600 °C calcined sample</td>
<td>582.2</td>
<td>2901.2</td>
<td>20.0%</td>
</tr>
<tr>
<td>700 °C calcined sample</td>
<td>220.0</td>
<td>2155.6</td>
<td>10.2%</td>
</tr>
<tr>
<td>800 °C calcined sample</td>
<td>38.0</td>
<td>896.6</td>
<td>4.2%</td>
</tr>
<tr>
<td>900 °C calcined sample</td>
<td>3.9</td>
<td>243.8</td>
<td>1.6%</td>
</tr>
</tbody>
</table>
Figure 7 shows the magnetization curves measured at 5 K for four nanoparticle samples. The specific saturation magnetizations measured at 5 and 300 K for these samples are summarized in Fig. 8. It can be seen from Figs. 7 and 8 that the specific saturation magnetization at both 5 and 300 K increased with calcination temperature. This is because the higher the calcination temperature, the more complete the conversion of Co-oxide to metallic Co. This result is consistent with that revealed by the exchange bias field data in Table I. For the nanoparticles calcined at 900 °C, the saturation magnetization 4πM_s was 9.17 KGs at 5 K and 9.07 KGs at 300 K, which is in good agreement with the expected values of 9.08 KGs at 0 K and 9.00 KGs at 293 K, respectively. This result further verifies that the pure Co nanoparticles with SiO_2 coating can be fabricated with the engineered wet chemical approach, and the SiO_2 coating has the ability of protecting Co nanoparticles from oxidation.

It also can be seen from Fig. 7 that the magnetization for the 600 °C calcined nanoparticles could not saturate even in a strong field of 55 K.Oe. This is believed to be due to: (1) the nonsaturation effect of the antiferromagnetic CoO and Co_3O_4 in the nanoparticles; and (2) the superparamagnetic behavior of some Co nanoparticles which had a very small effective size (because of the presence of the big Co-oxide core). However, the magnetization saturation for the nanoparticles prepared at 700, 800, and 900 °C are observed in Fig. 7. This is because the volume fractions of CoO and Co_3O_4 in these samples are relatively low.

Figure 8 shows the coercivity measured at 10 and 300 K as a function of calcination temperature. As shown in Fig. 9, the coercivity decreases with increasing calcination temperature. Since the Co phase in the nanoparticles calcined at lower temperature has a smaller effective size due to the presence of the inner Co-oxide core, it can be inferred from Fig. 9 that the coercivity decreased with increasing particle size. This result is consistent with the theoretical analysis given in Ref. 23, where R. C. O’Handley argued that the coercivity went as $H_c \approx a/r^2 - b/r$, particle size for noninteracting single-domain fine particles. The Co nanoparticles in our measurement samples are free from interaction, and their sizes are smaller than the single-domain critical size (76 nm) of fcc Co particles. It also can be seen from Fig. 9 that the coercivities measured at 10 K are notably higher than those measured at 300 K for the nanoparticles calcined at 600, 700, and 800 °C. This is believed to be due to the Co/CoO exchange coupling, which occurs at 10 K and disappears at 300 K. In addition, although the nanoparticles calcined at low temperatures exhibit high coercivities up to 984.3 Oe, the nanoparticles calcined at 900 °C exhibit low coercivities of 126.7 Oe at 10 K and 63.3 Oe at 300 K. This indicates that, using the engineered wet chemical approach, the magnetic softness of the nanoparticles can be readily controlled by the calcination temperature.

**IV. CONCLUSION**

SiO_2-coated Co nanoparticles were synthesized using the engineered wet chemical approach, and their structure was found to vary with calcination temperature. When the calcination temperature was as high as 900 °C, the nanoparticles exhibited a core/shell structure: the core was fcc Co and the
shell was amorphous SiO$_2$. When the calcination temperature was 800 °C or below, the nanoparticles had a nano-onion structure: the shells from the exterior to the interior were amorphous SiO$_2$, fcc Co, and CoO, and the very inner core was Co$_3$O$_4$. The size of the Co-oxide core decreased with increasing calcination temperature. Due to the non-saturation effect of the CoO and Co$_3$O$_4$ and the super-paramagnetic behavior of some small Co nanoparticles, the magnetization for 600 °C calcined nanoparticles did not saturate even in a strong field of 55 KOe. The saturation magnetization for 900 °C calcined nanoparticles was 9.17 KGS at 5 K and 9.07 KGS at 300 K, which is consistent with the expected values. At both low and room temperatures, the coercivity decreased with increasing calcination temperature, which can be explained by the size effect of Co nanoparticles. For the nanoparticles calcined at 800 °C or below, the low-temperature coercivity was found to be notably higher than the room-temperature one; this is believed to be due to the exchange coupling across the ferromagnetic Co/antiferromagnetic CoO interfaces.

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