Magnetic properties of CoFe$_2$O$_4$ nanoparticles synthesized through a block copolymer nanoreactor route

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The development of self-assembled magnetic CoFe$_2$O$_4$ nanoparticles within polymer matrices at room temperature is reported. Diblock copolymers consisting of poly (norbornene) and poly (norbornene-dicarboxylic acid) (NOR/NORCOOH) were synthesized. The self-assembly of the mixed metal oxide within the NORCOOH block was achieved at room temperature by processing the copolymer nanocomposite using wet chemical methods. Morphology and magnetic properties were determined by superconducting quantum interference device magnetometry, transmission electron microscopy, wide angle x-ray diffraction, and $^{57}$Fe Mössbauer spectroscopy. The CoFe$_2$O$_4$ nanoparticles are uniformly dispersed within the polymer matrix, and have an average radius of 4.8±1.4 nm. The nanocomposite films are superparamagnetic at room temperature and ferrimagnetic at 5 K. © 2002 American Institute of Physics. [DOI: 10.1063/1.1456258]

Magnetic properties of nanoparticles are subject to intense research activity driven by a fundamental interest in the novel physical properties of the nanoscale system and also potential industrial application of nanostructured materials. This letter reports on the magnetic properties of well-dispersed, CoFe$_2$O$_4$ nanoparticles within a polymer matrix. The use of diblock copolymer as a self-assembled nanotemplate enables us to synthesize magnetic nanoparticles at room temperature. Comparable inorganic methods for the synthesis of nanoscale mixed-metal oxides require heating at high temperatures in order to produce the desired oxide composition and microstructure. The development of such mixed-metal oxide polymer-based nanocomposites is targeting the functionalization into device technologies for high density memory and magnetic recording applications.

$[\text{NOR}]_{400}/[\text{NORCOOH}]_{50}$ diblock copolymers were synthesized by ring opening metathesis polymerization of norbornene (NOR) and norbornene trimethylsilane (NOR-COOTMS). The polymer was dissolved in THF, and FeCl$_3$ and CoCl$_2$ were mixed with the polymer solution (polymer:FeCl$_3$:CoCl$_2=1:25:0$; 12.5 mole). Due to the high affinity of these metals towards the COOH group, FeCl$_3$ and CoCl$_2$ were directly attached to the [NORCOOH] second block. Solid films were formed by static casting over a period of three days. The films were then washed with NaOH and water. FeCl$_3$ and CoCl$_2$ reacted with NaOH and water within the NORCOOH nanoreactors and formed CoFe$_2$O$_4$ nanocrystals.$^1$

Gel permeation chromatography (GPC) was performed with a Waters GPC 2000 with a series of Waters Styragel columns in conjunction with a Waters RI detector. The mobile phase was THF with a flow rate of 1.0 mL/min. The GPC columns were calibrated with polystyrene standards (Polymer Laboratories). The molecular weight of the diblock copolymer was thus determined to be 68 000 daltons with a polydispersity index of 1.2. The morphology of the polymer samples were studied using a HITACHI H-600 transmission electron microscope operated at 100 keV. Ultrathin (100 nm) samples for transmission electron microscopy observation were prepared with a diamond knife using an LKB Ultrotome III Model 8800. A transmission electron micrograph of the polymer (Fig. 1) shows the CoFe$_2$O$_4$ nanoparticles are oval shaped and have an average radius of 4.8±1.4 nm.

The structure of CoFe$_2$O$_4$ nanoparticles was characterized using a Bruker D8 Advance Powder x-ray diffractometer. Due to the large weight fraction of the amorphous polymer matrix (94.3%), the amorphous contribution dominated the scattering spectrum, and it was not possible to clearly discern the metal oxide contribution in the overall scattering of the nanocomposite. The polymer/metal oxide nanocomposite was thus heated at a temperature of 250 °C under a nitrogen atmosphere for 48 h to degrade the polymer. This temperature was chosen to be high enough to degrade the polymer matrix but low enough so that no solid state reaction occurs in the metal oxide. Since the temperature

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treatment was performed in an oxygen free atmosphere, the oxidation state of the metal oxide should not change. Once the amorphous matrix was removed, the scattering from the mixed-metal oxide particles was evident as shown in Fig. 2. The lattice spacing, \( d \), obtained from x-ray diffraction were compared to literature values for CoFe\(_2\)O\(_4\). The close match of our experimental values with literature values indicate successful room-temperature synthesis of CoFe\(_2\)O\(_4\) nanoparticles.

The magnetic properties of the block copolymer samples were measured using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The magnetic properties of the CoFe\(_2\)O\(_4\)-polymer nanocomposite are shown in Fig. 3. The measured magnetization \( M \) was divided by the total mass of the film used. At room temperature, the magnetization curve exhibits no hysteresis, indicating that the nanocomposite films are superparamagnetic. Both the remanence and coercivity are zero at 300 K. The magnetization, \( \sigma \), at an applied field of 50 kOe is 1.03 emu/g of the nanocomposite. \( \sigma = 1.03 \text{ emu/g} \) of the nanocomposite corresponds to 18.04 emu/g of CoFe\(_2\)O\(_4\), since the nanocomposite contains 5.7% CoFe\(_2\)O\(_4\) by weight. The nanocomposite films exhibit a remanence \( (\sigma_r) = 3.4 \times 10^{-2} \) emu/g and coercivity \( (H_c) = 100 \text{ Oe} \) at 77 K. The magnetization, \( \sigma \), at an applied field of 50 kOe is 2.12 emu/g of the nanocomposite corresponds to 37.19 emu/g of CoFe\(_2\)O\(_4\). Complete blocking of spin reversal occurs at 5 K and the nanocomposite films become ferrimagnetic. At this temperature, the coercivity, \( H_c \), is 5.3 kOe and the remanence, \( \sigma_r \), is 0.68 emu/g of nanocomposite, which is equivalent to 11.93 emu/g of CoFe\(_2\)O\(_4\). The magnetization \( (\sigma) \) at an applied field of 50 kOe is 3.25 emu/g corresponding to 57.1 emu/g of CoFe\(_2\)O\(_4\). The blocking temperature and the saturation coercivity were determined to be \( T_B(\text{Mag}) = 80 \text{ K} \) and \( H_c^0 = 6.1 \text{ kOe} \), respectively.

The most remarkable feature of the magnetization curves is that the magnetization data is far from saturation up to the highest field applied of 50 kOe, even at 300 K, which is above the blocking temperature of the sample. This is an indication of strong surface-spin pinning at the particle/support interface, resulting in a noncollinear spin structure within the CoFe\(_2\)O\(_4\) particles. Earlier studies on ferrite particles such as \( \gamma^{-}\text{Fe}_2\text{O}_3, \text{NiFe}_2\text{O}_4 \) (Ref. 7), and CoFe\(_2\)O\(_4\)
of the CoFe$_2$O$_4$ nanoparticles [Figs. 5(a) and 5(b)]. Table I gives the Mössbauer parameters obtained from least square fits of the spectra. The spectral features observed at 4.2 K are consistent with those previously reported for CoFe$_2$O$_4$ particles by other Mössbauer investigations.$^{8,10}$

CoFe$_2$O$_4$ nanoparticles have been synthesized using the self-assembled nanoscale morphologies of block copolymers as a template. Wide angle x-ray diffraction pattern along with the low temperature Mössbauer phase characterization confirms the formation of CoFe$_2$O$_4$ nanoparticles. The nanoparticles have a uniformly distributed oval shaped morphology with an average radius of 4.8±1.4 nm. Diblock copolymer-CoFe$_2$O$_4$ nanocomposites are superparamagnetic at room temperature and ferrimagnetic at 5 K. The magnetization of the nanocomposite remains unsaturated up to the highest field applied of 50 kOe. This is an indication of strong surface-spin pinning at the particle/support interface, resulting in a noncollinear spin structure within the CoFe$_2$O$_4$ particles. Earlier studies$^{11,12}$ suggest that a high temperature (>325 °C) annealing is necessary to synthesize superparamagnetic of CoFe$_2$O$_4$ nanoparticles. We succeeded in synthesizing such nanoparticles at room temperature. This indicates the efficiency of diblock copolymers as nanoreactors, inside which nanoparticles can be grown in a controlled manner.

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**Table I.** Mössbauer parameters for the diblock copolymer-CoFe$_2$O$_4$ nanocomposite.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Isomer shift$^a$ (mm/s)</th>
<th>$E_Q$ (mm/s)</th>
<th>$H_{hf}$</th>
<th>Fe(A)/Fe(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.27</td>
<td>0.72</td>
<td>⋯</td>
<td>0.59</td>
</tr>
<tr>
<td>4.2</td>
<td>0.39</td>
<td>⋯</td>
<td>501</td>
<td>0.73</td>
</tr>
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$^a$Isomer shifts are relative to metallic Fe at room temperature.

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