

Magnetic properties of CoFe_2O_4 nanoparticles synthesized through a block copolymer nanoreactor route

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The development of self-assembled magnetic CoFe_2O_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_2O_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_2O_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).¹ 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 $[\text{NORCOOH}]$ 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_2O_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 Ultratome III Model 8800. A transmission electron micrograph of the polymer (Fig. 1) shows the CoFe_2O_4 nanoparticles are oval shaped and have an average radius of 4.8 ± 1.4 nm.

The structure of CoFe_2O_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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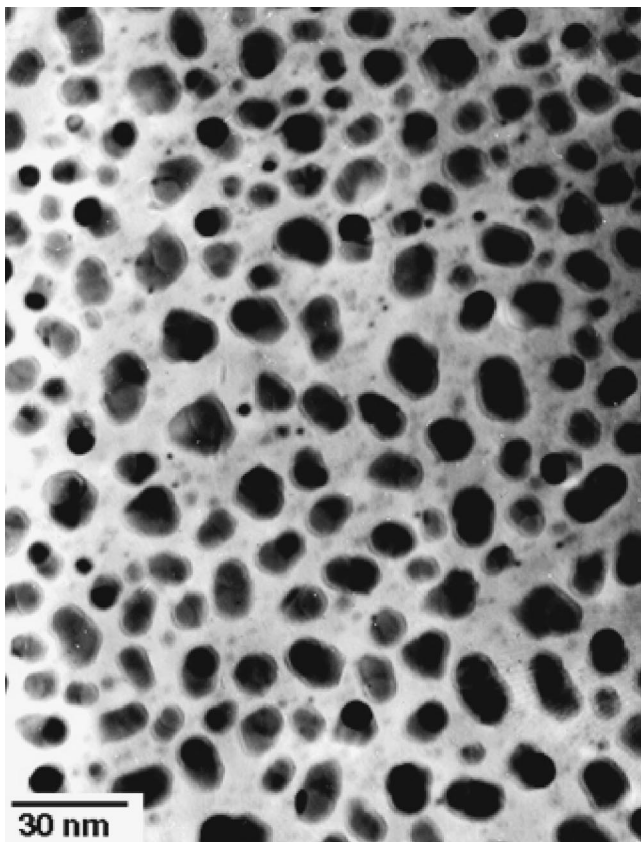


FIG. 1. Transmission electron micrograph of the diblock copolymer CoFe₂O₄ nanocomposite.

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^{2,3} for CoFe₂O₄. The close match of our experimental values with literature values indicate successful room-temperature synthesis of CoFe₂O₄ 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 CoFe₂O₄-polymer nanocomposite are shown in Fig. 3. The measured magnetization

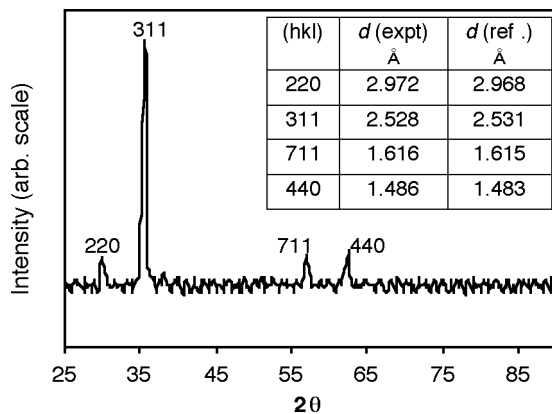


FIG. 2. Wide angle x-ray diffraction pattern of the polymer after heat treatment.

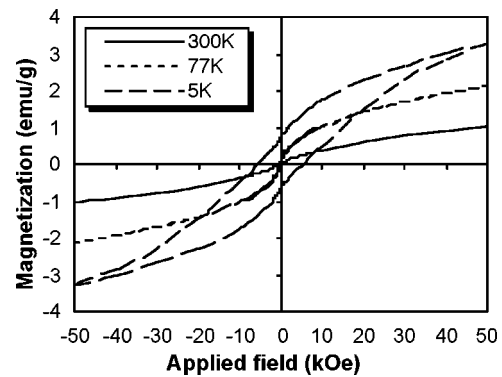


FIG. 3. Magnetization vs applied magnetic field for the block copolymer-CoFe₂O₄ nanocomposite at 300, 77, and 5 K.

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, σ , at an applied field of 50 kOe is 1.03 emu/g of the nanocomposite. $\sigma = 1.03$ emu/g of the nanocomposite corresponds to 18.04 emu/g of CoFe₂O₄, since the nanocomposite contains 5.7% CoFe₂O₄ by weight. The nanocomposite films exhibit a remanence (σ_r) = 3.4×10^{-2} emu/g and coercivity (H_c) = 100 Oe at 77 K. The magnetization, σ at an applied field of 50 kOe is 2.12 emu/g of the nanocomposite corresponds to 37.19 emu/g of CoFe₂O₄. 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, σ_r , is 0.68 emu/g of nanocomposite, which is equivalent to 11.93 emu/g of CoFe₂O₄. The magnetization (σ) at an applied field of 50 kOe is 3.25 emu/g corresponding to 57.1 emu/g of CoFe₂O₄. The blocking temperature and the saturation coercivity were determined to be $T_B(\text{Mag}) = 80$ K and $H_c^0 = 6.1$ 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 CoFe₂O₄ particles. Earlier studies on ferrite particles such as γ -Fe₂O₃,⁴⁻⁶ NiFe₂O₄ (Ref. 7), and CoFe₂O₄

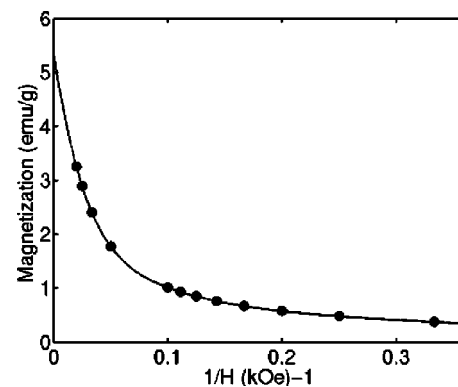


FIG. 4. Magnetization of the nanocomposite film as a function of inverse field extrapolated to infinite applied field. The solid line is a spline curve fit through the experimental points.

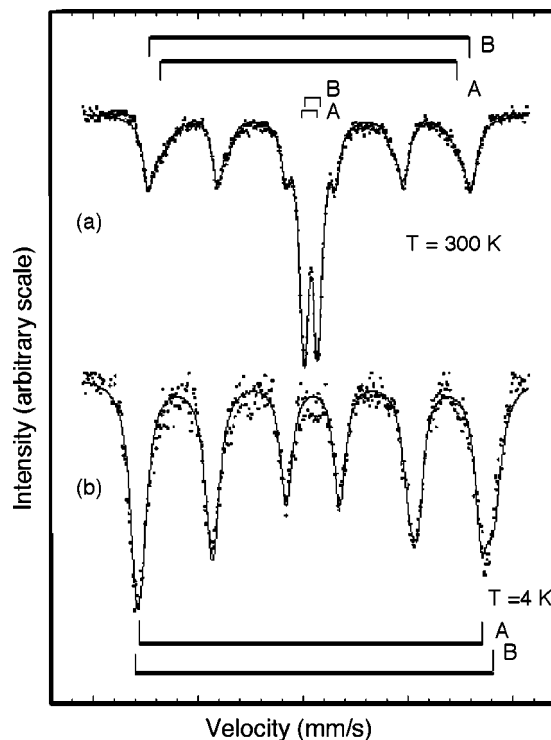


FIG. 5. Mössbauer spectra of a polymer- CoFe_2O_4 nanocomposite (a) at 300 K and (b) 4.2 K. The solid line represents a least-square fit to the experimental data.

(Ref. 8) have provided experimental evidence of presence of surface-spin pinning in small magnetically ordered systems. In Fig. 4, the magnetization data of the film at $T=5$ K is plotted as a function $1/H_{\text{appl}}$ and extrapolated to $1/H_{\text{appl}} \rightarrow 0$. We can thus obtain an estimate of the saturation magnetization of the film of 5.33 emu/g of film. This translates to $M_s = 93.5$ emu/g of CoFe_2O_4 which constituted 5.7% of film by weight. This value of M_s equals that of bulk CoFe_2O_4 at 5 K, ($M_{s,\text{bulk}} = 93.9$ emu/g).

The Mössbauer spectra of the block copolymer films were obtained using a conventional constant acceleration Ranger Electronics Corporation Mössbauer spectrometer, driven by a triangular wave form. The source was ^{57}Co in a Rh matrix maintained at room temperature. The CoFe_2O_4 block copolymer films were studied at 300 and 4.2 K (Fig. 5). The room temperature spectra are complex. They exhibit a quadrupolar component at the center of the spectrum and a magnetically split component spread across the spectrum. The presence of both the quadrupole and magnetic splitting is due to the existence of a size distribution ($r = 4.8 \pm 1.4$ nm) in the nanocomposite. This observation is similar to what is reported by Dorman *et al.*⁹

At room temperature, the quadrupole splitting dominates the magnetic splitting, and hence the sample becomes superparamagnetic. The intensity of the quadrupole splitting decreases with temperature. At 4.2 K, only the magnetic splitting is present and the CoFe_2O_4 block copolymer is completely ferrimagnetic. Thus, the Mössbauer spectra and the SQUID data provide complimentary information on the magnetic properties of the nanoparticles.

The room temperature and the 4.2 K spectra were analyzed further to investigate the magnetic hyperfine structure

TABLE I. Mössbauer parameters for the diblock copolymer- CoFe_2O_4 nanocomposite.

T (K)	Isomer shift ^a (mm/s)	E_Q (mm/s)	H_{hf}	Fe(A)/Fe(B)
300	0.27	0.72	...	0.59
	0.41	0.67	...	
	0.27	...	440	0.68
	0.41	...	447	
4.2	0.39	...	501	0.73
	0.53	...	526	

^aIsomer shifts are relative to metallic Fe at room temperature.

of the CoFe_2O_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_2O_4 particles by other Mössbauer investigations.^{8,10}

CoFe_2O_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_2O_4 nanoparticles. The nanoparticles have a uniformly distributed oval shaped morphology with an average radius of 4.8 ± 1.4 nm. Diblock copolymer- CoFe_2O_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_2O_4 particles. Earlier studies^{11,12} suggest that a high temperature (>325 °C) annealing is necessary to synthesize superparamagnetic of CoFe_2O_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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