Controlled Room Temperature Synthesis of $CoFe_2O_4$ Nanoparticles through a Block Copolymer Nanoreactor Route

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ABSTRACT: The synthesis and characterization of well-dispersed, $CoFe_2O_4$ nanoparticles within a polymer matrix at room temperature are reported. Comparable inorganic synthetic methods require heating at high temperatures in order to produce this particular mixed-metal oxide composition. Our modification of prior reported templating schemes using block copolymers consists of introducing a mixture of metal salts to a polymer solution before any microphase separation of the block copolymer constituents can occur, thus allowing fast diffusion of metals to the functional polymer backbone. The diblock copolymer matrix was synthesized using ring-opening metathesis polymerization of norbornene derivatives. The self-assembly of the mixed-metal oxide within the polymer template was achieved at room temperature by introducing a mixture of $FeCl_3$ and $CoCl_2$ into one of the functional polymer blocks and by subsequent processing of the copolymer by wet chemical methods to substitute the chlorine atoms with oxygen. $CoFe_2O_4$ nanoparticles were thus formed within the spherical microphase-separated morphology of the diblock copolymer, which serves as the templating medium. Transmission electron microscopy, Fourier transform infrared spectroscopy, and wide-angle X-ray diffraction were used to characterize the nanocomposite morphology, oxide chemical composition, and process of oxide formation.

1. Introduction

Metal oxide nanoparticles are the subject of current interest because of their unusual optical, electronic, and magnetic properties. The spatial confinement of electronic and vibrational excitations results in a widening of the energy band gap and observation of quantum size effects. Quantum size effects and large surface-to-volume ratios can contribute to unique properties[1,2] of nanoconfined metal oxides, which often differ from bulk properties. For example, below a critical size, magnetic particles become a single magnetic domain and are superparamagnetic.[3] Cobalt ferrite, $CoFe_2O_4$, is a well-known hard magnetic material with very high cubic magnetocrystalline anisotropy, high coercivity, and moderate saturation magnetization. These properties make it a promising material for high-density magnetic recording.

This paper reports on the synthesis and characterization of well-dispersed, $CoFe_2O_4$ nanoparticles within a polymer matrix at room temperature. Comparable inorganic methods for synthesis of nanoscale mixed-metal oxides require heating at high temperatures in order to produce the desired oxide composition and microstructure. Single-metal nanoclusters of Cu, Ag, Pd, and Pt and metal oxide nanoparticles of Fe_2O_3 and CuO have been recently synthesized within microphase-separated domains of diblock copolymers[4−7] using templating methods. The modification employed in this research consists of introducing mixture of metal salts to the polymer solution before any microphase separation of the block copolymer constituents can occur, thus allowing fast diffusion of metals to the functional polymer backbone. The self-assembly of the oxide within the diblock copolymer matrix was achieved at room temperature by introducing $FeCl_3$ and $CoCl_2$ precursors into one of the polymer blocks and by subsequent processing of the copolymer by wet chemical methods to substitute the chlorine atoms with oxygen. $CoFe_2O_4$ nanoparticles are thus formed within the spherical microphase-separated morphology of a block copolymer, which serves as the templating medium. The development of such mixed-metal oxide polymer-based nanocomposites is targeting the functionalization into device technologies.

2. Experimental Section

Norbornene (NOR), anhydrous tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) were purchased from Aldrich and were used without any further purification. NORCOOH (2-norbornene-5,6,-dicarboxylic acid) and NORCOOTMS (2-norbornene-5,6,-dicarboxylic acid bis(trimethylsilyl) ester) were prepared according to literature procedures.[8] A Grubbs catalyst (bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride) for the polymerization was purchased from Strem Chemicals. Stock solutions (30 mg/mL) of the catalyst was prepared by dissolving the catalyst in THF and CH_2Cl_2.

NOR/NORCOOH diblock copolymers were synthesized by ring-opening metathesis polymerization (ROMP) of norbornene (NOR) and norbornene trimethylsilane (NORCOOTMS) (Figure 1). The Grubbs catalyst was used to initiate the polymerization. This catalyst has high tolerance toward impurities and hence enabled the use of commercially available norbornene without any further purification. 4% solution of norbornene in THF was prepared by dissolving 1 g of NOR (5.5×10^{-3} mol, 400 equiv) in 25 mL of THF. The polymerization was initiated by adding 0.75 mL (13.75×10^{-6} mol, 1/400 equiv) of catalyst solution. NORCOOTMS solution (44×10^{-3} mol, 50 equiv) was added to the living polymer solution after 1 h. The reaction was terminated after 24 h. The resultant $[NOR]_{400}/[NORCOOTMS]_{50}$ diblock was converted to $[NOR]_{400}/[NORCOOH]_{50}$ by precipitating the polymer solution in a mixture of methanol, acetic acid, and water. The block copolymers were dried under vacuum before static film casting. The $[NOR]_{400}/[NORCOOH]_{50}$ diblock was dissolved in THF, and $FeCl_3$ and $CoCl_2$ were mixed with the polymer solution (polymer:$FeCl_3$:

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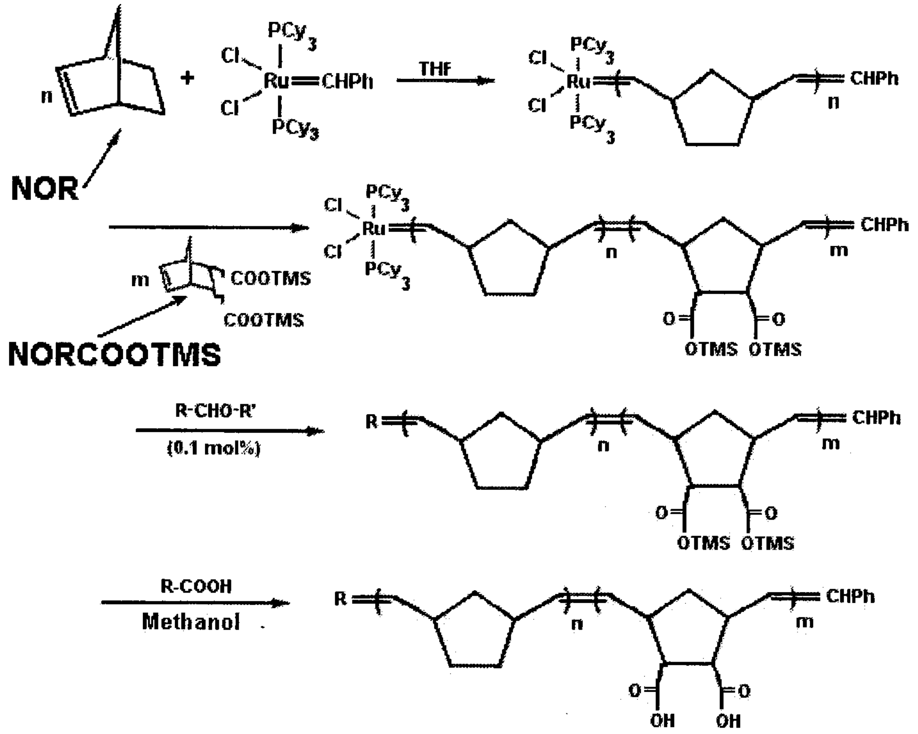

Figure 1. Ring-opening metathesis polymerization synthesis of the $[NOR]_{400}[NORCOOH]_{50}$ diblock copolymer.

$CoCl_2$ = 1:25.0:12.5 mol). Because of the high affinity of these metals toward the COOH group, $FeCl_3$ and $CoCl_2$ were preferentially attached to the [NORCOOH] second block. Solid films were formed by static casting over a period of 3 days. The films were then washed with NaOH and water. $FeCl_3$ and $CoCl_2$ reacted with NaOH and water and converted to $CoFe_2O_4$ nanocrystals within the self-assembled NORCOOH nanospheres of the diblock copolymer matrix.

The morphology of the polymer nanocomposites was studied using a HITACHI H-600 transmission electron microscope (TEM) operated at 100 keV. Samples for TEM were prepared by two different methods: $[NOR]_{400}[NORCOOH]_{50}-CoFe_2O_4$ nanocomposites were embedded in epoxy, and ultrathin (100 nm) samples for TEM observation were prepared with a diamond knife using an LKB Ultratome III model 8800. In order to study the morphology of the polymer doped with $FeCl_3$ and $CoCl_2$ before the formation of the mixed-metal oxide, 600 mesh copper TEM grids were placed in a desiccator together with one drop of 0.1% metal doped polymer solution. A small dish filled with 20 mL of THF was placed in the desiccator in order to reduce the rate of solvent evaporation from the polymer solution. The crystal structure of the $CoFe_2O_4$ nanoparticles was characterized using wide-angle X-ray diffraction. The diffraction pattern was recorded by a Bruker D8 Advance powder X-ray diffractometer using Cu Kα radiation. The process of nanoparticle formation was studied using a Nicolet series II Magna-IR 550 FTIR spectrometer.

3. Results and Discussion

Diblock copolymers of $(NOR)_m/(NORCOOH)_n$ were synthesized with m/n ratios of 400/50 using ring-opening metathesis polymerization (ROMP) with a ruthenium-based catalyst developed by Grubbs. ROMP is advantageous because it results in a narrow molecular weight distribution of the polymer, which is important in this templating application in order to produce uniformly sized nanostructures. ROMP also allows the presence of specific functional groups on monomers during polymerization, which other polymerization processes might not tolerate. Based on the chosen volume fractions of the two blocks of the copolymer, a spherical nanoparticle morphology was targeted for this work.

A schematic representation for the self-assembly of magnetic mixed-metal oxide nanostructures using the block copolymer templating strategy is shown in Figure 2. In our work, the templating is different from previous reports in that the metal salt is introduced while the polymer is in solution, before any microphase separation of the two blocks can occur. Earlier block copolymer nanoreactor synthesis schemes[4-7] have introduced a single metal salt solution into spin-cast or static-cast microphase-separated solid diblock copolymers films. The advantages which our modified templating process presents are a rapid diffusion and attachment of the metal to the polymer since both are in the liquid state and resultant self-assembled nanostructures at room temperature through wet chemical methods. This modification could help achieve a more commercially attractive process integration in the fabrication of novel magnetic devices, without requiring additional thermal cycling steps.

FTIR was used to verify the ion exchange between the $FeCl_3$, $CoCl_2$ metal salts, and the COOH functional group which is present on one of the blocks of the copolymer. Spectra were collected for polymer solutions in THF as well as solid films of pure and metal-doped diblock copolymers. Parts a and b of Figure 3 show the FTIR spectra of undoped and metal doped (with $FeCl_3$ and $CoCl_2$) $[NOR]_{400}[NORCOOH]_{50}$ solutions in THF, respectively. In the undoped polymer solution the carboxylic acid carbonyl peak is located at 1720 cm^{-1}.[9] After doping with the mixture of metal chloride solutions, the peak at 1720 cm^{-1} disappears and a new peak at 1620 cm^{-1} appears, which is associated with asymmetric stretching of carboxylate salts. The upfield shift on the FTIR spectrum of the carbonyl peak verifies the association of the Fe^{3+} and Co^{2+} cations to the carboxylate groups present on one of the blocks of the copolymer.[7]

The FTIR spectra presented in Figure 4 were collected after static casting a solid nanocomposite film. These spectra indicate that after the solid film formation the

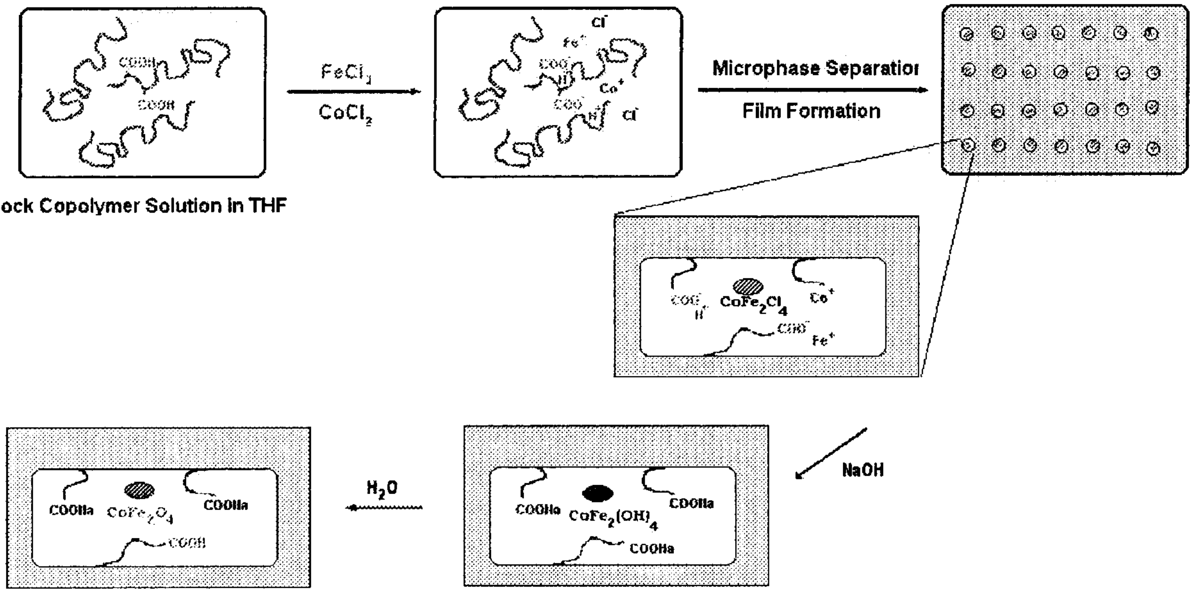

Figure 2. Schematic of $CoFe_2O_4$ nanoparticle formation within the diblock copolymer.

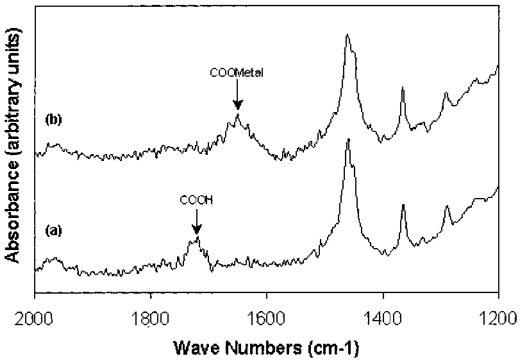

Figure 3. FTIR spectra of diblock copolymer solutions in THF (a) undoped and (b) after doping with $FeCl_3$ and $CoCl_2$.

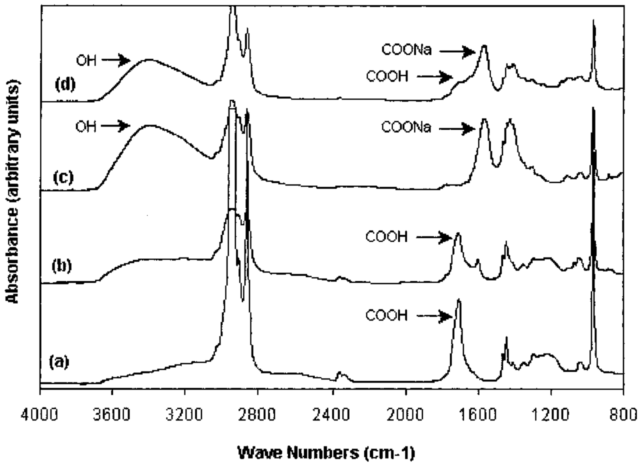

Figure 4. FTIR of static cast solid diblock copolymer films (a) undoped, (b) after doping with $FeCl_3$ and $CoCl_2$, (c) after the NaOH wash, and (d) after the final H_2O wash.

carboxylic acid peak at 1710 cm^{-1} reappears, and the intensity of the carboxylate peak at 1605 cm^{-1} decreases significantly (Figure 4b). After washing with NaOH, the peaks at 1710 and 1605 cm^{-1} disappear, and a new peak at 1556 cm^{-1} appears (Figure 4c), which is associated with the formation of COONa.[10] The disappearance of the peak at 1605 cm^{-1} indicates that the Fe^{3+} and Co^{2+} cations are no longer associated with the polymer matrix. This alkali base has thus been effective in the process of metal cation to oxide conversion. After subsequent washing with water, the intensity of the COONa peak (1556 cm^{-1}) disappears and a small peak at 1710 cm^{-1} reappears, indicating that some of the COONa has been transformed back to free COOH groups (Figure 4d).

The peaks at 3400 cm^{-1} on the FTIR spectra represent the stretching of the OH group present on the carboxylic acid. The occurrence of this peak in the NaOH (Figure 4c) and H_2O (Figure 4d) washed samples show the carboxylic acid proton is indeed regenerated. The undoped block copolymer solid films (Figure 4a) also show the hydroxyl peak at 3400 cm^{-1}.

This indicates that although some of the metals are still associated with the carboxylate group, most of the metals are no longer coordinated with the polymer backbone, as soon as the solid polymer is formed.

A transmission electron micrograph of the polymer film doped with $FeCl_3$ and $CoCl_2$ (Figure 5) shows presence of metal nanoparticles. This TEM complements the FTIR evidence and verifies the disassociation of the metals with the polymer backbone. After washing with NaOH and water, any remaining metal–polymer bonds are broken and chlorine atoms are substituted with oxygen. This leads to the formation of the mixed-metal oxide $CoFe_2O_4$ nanoparticles. The TEM image (Figure 5b) shows that the $CoFe_2O_4$ nanoclusters produced by this process are oval-shaped and have an average radius of 4.8 ± 1.4 nm.

Wide-angle X-ray diffraction was used to characterize the specific crystal structure of $CoFe_2O_4$ nanoparticles. Because of 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 treatment was performed in an oxygen-free atmosphere, the oxidation

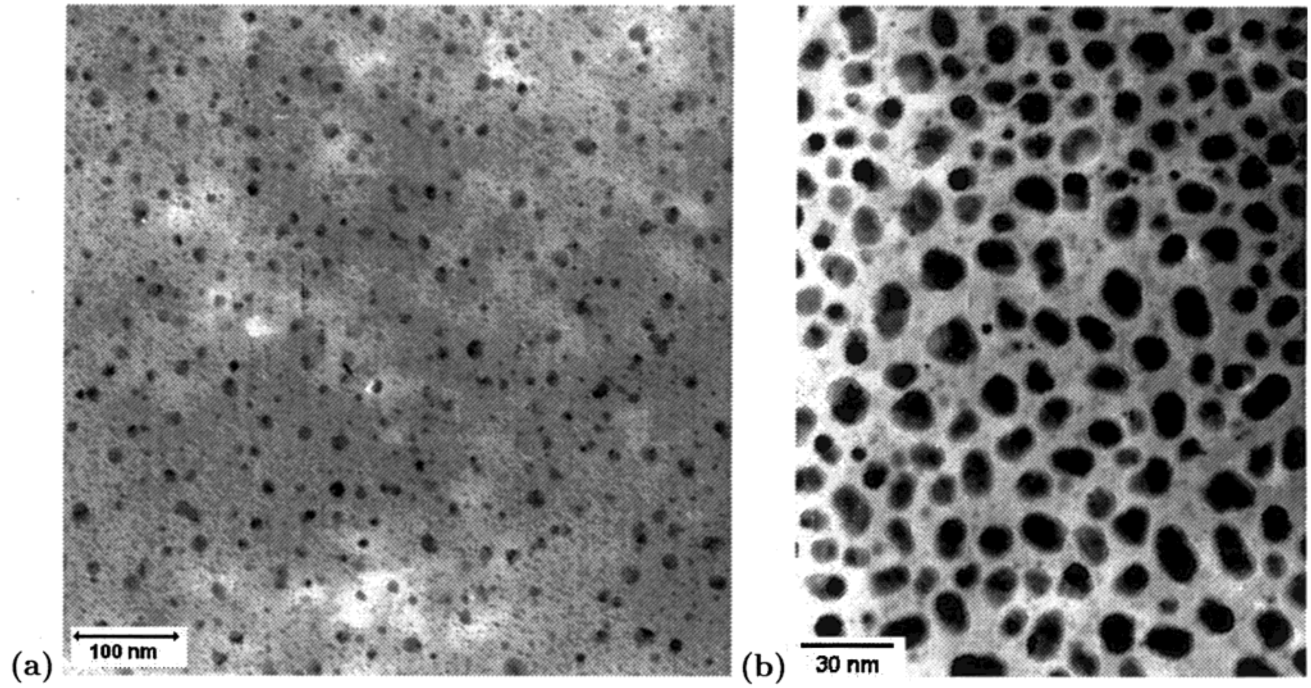

Figure 5. Transmission electron micrograph of (a) diblock copolymer doped with $FeCl_3$ and $CoCl_2$ and (b) copolymer−$CoFe_2O_4$ nanocomposite.

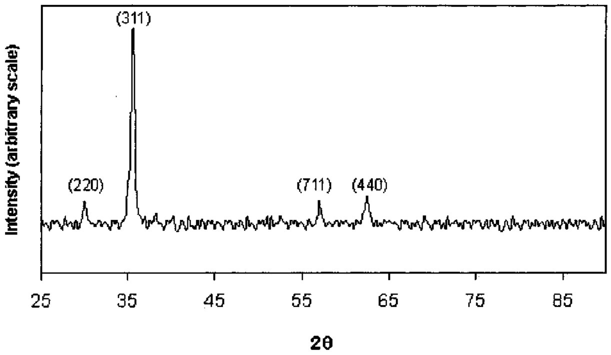

Figure 6. Wide-angle X-ray diffraction pattern of the nanocomposite after the heat treatment.

Table 1. X-ray Diffraction Data

(*hkl*)	*d* (experiment), Å	*d* (literature[11]), Å
220	2.972	2.968
311	2.528	2.531
711	1.616	1.615
440	1.486	1.483

state of the metal oxide should not change. Figure 6 shows the X-ray diffraction pattern of the material after the heat treatment. Once the amorphous matrix is removed, the scattering from the mixed-metal oxide nanoparticle is evident. The lattice spacings, *d*, obtained from X-ray diffraction are compared to literature values for $CoFe_2O_4$ in Table 1. The close match of our experimental values with literature values indicates successful room temperature synthesis of $CoFe_2O_4$ nanoparticles.

4. Conclusions

$CoFe_2O_4$-doped diblock copolymers of $[NOR]_{400}/[NOR\text{-}COOH]_{50}$ show a uniformly distributed oval-shaped morphology with an average radius of 4.8 ± 1.4 nm. We succeeded in synthesizing such nanoparticles at room temperature with uniform shape and distribution. Earlier studies on inorganic synthesis of $CoFe_2O_4$ nanoparticles[12,13] suggest that it is necessary to anneal the nanoparticles at a high temperature (325 °C) in order to produce the same magnetic oxide composition that we achieved at room temperature. The current work thus indicates the efficiency of diblock copolymers as nanoreactors, inside which nanoclusters can be grown in a controlled manner at low temperatures.

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References and Notes

(1) Halperin, W. P. *Rev. Mod. Phys.* **1986**, *58*, 533.
(2) Kresin, V. V. *Phys. Rep.* **1992**, *220*, 1.
(3) Bean, C. P.; Livingstone, J. D. *J. Appl. Phys.* **1959**, *30*, 120.
(4) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 24.
(5) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *J. Am. Chem. Soc.* **1992**, *114*, 7295.
(6) Ng Cheong Chan, Y.; Craig, G. S. W.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 885.
(7) Sohn, B. H.; Cohen, R. E. *Chem. Mater.* **1997**, *9*, 264.
(8) Royappa, A. T.; Saunders, R. S.; Rubner, M. F.; Cohen, R. E. *Langmuir* **1998**, *14*, 6207.
(9) *The Aldrich Library of FT-IR Spectra*, 1st ed.; Pouchert, C. J., Ed.; Aldrich Chemical Co.: Milwaukee, WI, 1985; Vol. 1, p 491A.
(10) *The Aldrich Library of FT-IR Spectra*, 1st ed.; Pouchert, C. J., Ed.; Aldrich Chemical Co.: Milwaukee, WI, 1985; Vol. 1, p 545A.
(11) *Standard X-Ray Diffraction Powder Patterns*; Swanson, H. E., McMurdie, H. F., Morris, M. C., Evans, E. H., Paretzkin, B., Eds.; National Bureau of Standards: Washington, DC, 1971; Mono. 25, Sec. 9, p 22.
(12) Grigorova, M.; Blythe, H. J.; Blaskov, V.; Rusanov, V.; Petkov, V.; Masheva, V.; Nihtianova, D.; Martinez, L. M.; Munoz, J. S.; Mikhov, M. *J. Magn. Magn. Mater.* **1998**, *183*, 163.
(13) Moumen, N.; Veillet, P.; Pileni, M. P. *J. Magn. Magn. Mater.* **1995**, *149*, 67.

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