Magnetic Properties and Mössbauer Spectroscopy of Fe₃O₄/CoFe₂O₄ Nanorods

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ABSTRACT: Fe₃O₄/CoFe₂O₄ nanorods were obtained via a simple seed mediated synthesis. Nanorods were used as seeds to grow CoFe₂O₄ by thermal codecomposition of the cobalt(II) and iron(III) acetylacetonate precursors. The growth process was monitored by electron microscopy (SEM, TEM), and the resulting nanorods were characterized by powder X ray diffraction analysis and IR and Raman spectroscopy. Magnetometry and AC susceptometry studies revealed a distribution of Néel relaxation times with an average blocking temperature of 140 K and a high field magnetization of 42 Am²/kg. Complementarily recorded ⁵⁷Fe−Mössbauer spectra were consistent with the Fe₃O₄/CoFe₂O₄ spinel structure and exhibited considerable signs of spin frustration, which was correlated to the internal and surface structure of the nanorods.

INTRODUCTION

Magnetic nanoparticles (MNPs) reveal interesting size and material dependent properties and have attracted great interest for application in various fields¹–³ including catalysis⁴,⁵ theranostics⁶,⁷ magnetooptics⁸–¹⁰ and magneto rheology.¹¹,¹² To obtain uniform MNPs with a defined size, shape, and composition, various methods have been established, including cation/anion exchange,¹³ coprecipitation,⁴,¹⁴ thermal decomposition,¹⁵–¹⁸ microemulsions,¹⁹ and hydrothermal/solvothermal synthesis.¹⁰ In order to obtain monodisperse MNPs, these methods typically separate the nucleation and growth phases into either several temporal or spatial steps.¹² The latter seed mediated growth process usually leads to core/shell nanoparticles.²² CoFe₂O₄ (CFO) is a material displaying an inverse spinel structure (i.e., in which Co²⁺ ions preferably occupy the octahedral spinel B sites) and a high chemical and physical stability. The energy for preferential occupation of the octahedral sites in the spinel lattice, however, is relatively small for Co²⁺ compared to other M²⁺ ions. Depending on the synthesis procedure and the number of lattice defects, different degrees of inversion are obtained, i.e., ranging from random Co²⁺ distribution to its preferential occupation of the B site sublattice.²³ Co²⁺ (~3 μB) has a lower atomic magnetic moment than Fe³⁺ (~5 μB), and hence, the magnetic properties will also depend on the degree of inversion. Bulk saturation magnetizations (Mₛ) of 80 Am²/kg have been reported for CFO, which is slightly lower than that of magnetite (Fe₃O₄, Mₛ ~89 Am²/kg), combined with an unusually high magnetocrystalline anisotropy of ~2 × 10⁵ J/ m¹.²⁴ In CoₓFe₂−ₓO₄, the magnetocrystalline anisotropy depends on the level of Co²⁺ doping, where larger amounts of Co²⁺ result in higher magnetic anisotropy and coercivity, until a maximum is reached at approximately x = 0.6.²⁵,²⁶ The Curie temperature (T_C) for CFO nanoparticles is about 670 K and decreases with an increasing level of Co²⁺ doping.²⁵–²⁹ CFO MNPs are particularly appealing materials for various fields of application, and a variety of procedures has been developed, e.g., for the synthesis of spherical or cube shaped CFO MNPs, finely tuned with respect to size, shape, and Co stoichiometry.³⁰ Reports on the preparation of CFO particles with anisotropic morphology such as nanorods or nanowires, however, are scarce, although the anisotropic MNPs have promising advantages over the spherical shape (e.g., the stronger induced magnetic field).³¹ CFO based nanorods should show an Mₛ comparable to Fe₃O₄; however, the coercivity and the magnetic blocking temperature (T_B) should be significantly increased due to a higher spin–orbit coupling. Due to the symmetric, cubic crystal structure of CFO, it seems to be challenging to control the anisotropic growth of CFO
into small, rod-like structures. In order to break the structural symmetry, polymers or soft, micellar templates have been employed to induce anisotropic CFO growth. Large CFO nanowires with widths of 100 nm, for example, were prepared via a sol–gel approach using poly(vinylpyrrolidone) as a surfactant.\textsuperscript{32} CFO nanowires with lengths of several micrometers were also synthesized via microemulsion techniques.\textsuperscript{33} Hydrothermal synthesis led to bundles of CFO nanorods with a length of 120 nm.\textsuperscript{34} Rod-like CFO MNPs (lengths 80–160 nm; average width 43 nm) were obtained by coprecipitation and subsequent annealing, in the presence of some remaining spherical MNPs.\textsuperscript{35} In general, these procedures typically result in the formation of rather large CFO rods, and to the best of our knowledge, no synthetic routes are available for CFO based nanorods with dimensions in the lower nanometer range (1–100 nm).

In the present work, we address the seed mediated synthesis of small, 51 nm long Fe_{3}O_{4}/CoFe_{2}O_{4} nanorods, where nanorods of well defined size and shape were used as seeds to direct the epitaxial growth of CFO. The structure and magnetic properties of the seeds and the Fe_{3}O_{4}/CFO nanorods were characterized via scanning and transmission electron microscopy (SEM, TEM), powder X-ray diffraction analysis (XRD), IR and Raman spectroscopy, and temperature dependent magnetization measurements following the zero-field cooled field cooled (ZFC/FC) protocol, and temperature dependent Mössbauer spectroscopy ($T = 4.3–293$ K), including experiments in external magnetic fields. The influence of the CFO layer on the magnetic properties was investigated.

**EXPERIMENTAL PROCEDURES**

**Chemicals.** Acetone anhydrous (99.9%), cobalt(II) acetylacetonate (Co(acac)$_2$, 97%), diphenyl ether (99%), 1,2 hexanediol (90%), hexadecylamine (99%), n-hexane anhydrous (95%), iron(III) acetylacetonate (Fe(acac)$_3$, 97%), iron(0) pentacarbonyl (Fe(CO)$_5$, 99.99%), 1 octanol (99%), oleic acid (90%), and oleylamine (70%) were purchased from Sigma Aldrich GmbH (Steinheim, Germany). Ethanol (99%) was purchased from Merck Chemicals GmbH (Darmstadt). All chemicals were used as received.

**Synthesis of Seeds.** Hexadecylamine (0.20 g) and oleic acid (2.00 mL) were dissolved in 1 octanol (8 mL) at 50 °C. After 10 min while stirring at 50 °C, the solution was cooled to ambient conditions and transferred to an autoclave reactor (20 mL, PTFE inlet), and Fe(CO)$_5$ (2.10 mL) was added. The autoclave was closed and transferred to an autoclave reactor (20 mL, PTFE inlet), and the heating program was started (20 °C to 100 °C, 1), (2) 100 °C to 230 °C (heating rate 7.5 °C min$^{-1}$) (3) 200 °C (30 min), (4) 200 °C to 230 °C (heating rate 7.5 °C min$^{-1}$) (5) 230 °C to 200 °C (heating rate 7.5 °C min$^{-1}$) (6) 230 °C (30 min). The argon power was used was 50 W. The samples were focused and the backscattered light, an MLPLAN 20x objective, NA 0.45 (Olympus, Tokyo, Japan), was applied. Spectra were measured over 60 s with three coadditions (3 x 20s). Powder XRD measurements were performed with a PANalytical X'Pert Pro X ray diffractometer employing Bragg–Brentano geometry with Cu Kα radiation and a Ni filter. The diffractograms were recorded over a period lasting 16 h at room temperature. The reflections were compared to reference data reported in the Joint Committee of Powder Diffraction Standards (JCPD) database. Magnetization measurements were performed at 5–400 K and 10 mT following the zero-field cooled field cooled protocol and field dependently at 5 and 300 K and field amplitudes up to 9 T to study the particles’ relaxation dynamics and static magnetic properties using the vibrating sample magnetometer (VSM) option of a Quantum Design PPMS DynaCool. To study nanoparticle relaxation behavior more closely, the nanorods were dispersed in Edwards L9/LP4/ KoratinSH (volume ratio 18/1/1) for an in depth AC susceptometry analysis at temperatures of 5–330 K in 10 K steps and frequencies of 0.1–1500 Hz using eight equidistant frequencies per magnitude with a Quantum Design MPMS SS SQUID magnetometer with an integrated AC option. Mössbauer spectra were recorded in transmission geometry and constant acceleration mode utilizing 20–70 mcg Co(Rb) sources. A 1 He bath cryostat was used to attain temperatures of 4.8–300 K and record spectra without external fields to study the sample’s general structure and magnetic phase transitions, while a reference spectrum of the dispersed nanorod sample was recorded at 4.8 K in a magnetic field of 5 T applied parallel to the y-ray propagation direction to obtain more detailed information regarding magnetic structure and spin canting effects.

**RESULTS AND DISCUSSION**

**Synthesis of Magnetic Nanorods.** The Fe$_3$O$_4$/CFO nanorods were synthesized by several steps of seed mediated growth. Initially, the seeds were prepared by decomposition of iron pentacarbonyl according to a procedure previously described by others.\textsuperscript{36,37} This procedure results in a mixture of the elongated target seeds and large spherical Fe$_3$O$_4$ MNPs.\textsuperscript{36} These 50–500 nm spherical MNPs have a $M$$_c$ of 75 Am$^2$/kg, whereas the $M$$_s$ of the seeds is 0.5 Am$^2$/kg and rather low. It is important to note that the procedure was optimized here to yield exclusively the target seeds as a pure product and no spherical MNPs. Figure 1A and B show the corresponding SEM and TEM micrographs of the pure seeds.
The mean size of the seeds is $57.2 \pm 17.8$ nm $\times$ 7.1 nm (±2.5). The seeds were then employed to obtain the Fe$_3$O$_4$/CFO nanorods via decomposition of the iron(III) acetylacetonate and cobalt(II) acetylacetonate precursors. At temperatures above 240 °C, the seeds were transformed into spherical MNPs, and thus, it is important to keep the reaction temperature below 240 °C during CFO coating. It was previously shown that the thermal decomposition of Fe(III) and Co(II) acetylacetonate precursors in high boiling point solvents yields CoFe$_2$O$_4$ particles with high $M_s$. In our case, however, one growth cycle neither resulted in a thick CFO layer nor did it significantly improve the magnetic properties of the nanorods. An increase in temperature may result in the growth of thicker CFO layers, but as mentioned above, the nanorods decompose into spherical MNPs at higher temperatures. Therefore, the CFO growth procedure was consecutively repeated three times to obtain nanorods with a distinct CFO layer. Any small spherical MNPs, which formed as byproducts during CFO growth, were separated from the Fe$_3$O$_4$/CFO nanorods via size selective precipitation in consecutive steps of suspension in chloroform and precipitation with acetone. Size selective precipitation techniques have been previously reported to narrow the size distribution of nanoparticles. In this procedure, an antisolvent is added to the suspended MNPs, leading to destabilization and precipitation of larger particles while the smaller ones remain in suspension. Figure 1C and D show the corresponding SEM and TEM images of the Fe$_3$O$_4$/CFO nanorods. The mean size of the Fe$_3$O$_4$/CFO nanorods is $51.2 \pm 16.5$ nm $\times$ 9.5 nm (±2.2). Characterization via ICP-OES, XRD, IR, and Raman Spectroscopy. After three cycles of CFO coating, the Fe$_3$O$_4$/CFO nanorods seemed to be slightly shorter than their original seeds, which might be a consequence of the nanorod workup after synthesis. The Co and Fe content of the Fe$_3$O$_4$/CFO nanorods was determined by ICP OES analysis to 13.1 and 48.0 wt %, respectively. This was further supported by SEM EDX analysis. It has to be noted that the original seeds contained only iron (29.6 wt %).

XRD analysis of the Fe$_3$O$_4$/CFO nanorods reveals broad reflections of low intensity, which are characteristic for small, rod-like nanoparticles (Figure 2 A). The Fe$_3$O$_4$/CFO nanorods show the reflections characteristic of the cubic Fe$_3$O$_4$ or CoFe$_2$O$_4$ phase, which are similar in lattice constants (JCPD 03 065 3107 or JCPD 00 022 1086: 30.1° (220), 35.4° (311), 43.1° (400), 57.0° (511), 62.6° (440), 74.0° (533), 89.7° (731) (2θ)). No reflections remain unassigned, which indicates that the Fe$_3$O$_4$/CFO nanorods are indeed composed of ferrite (Fe$_3$O$_4$ and/or CoFe$_2$O$_4$). The diffractograms of the initial seeds revealed broad reflections at 17°, 34° (major reflection), 39°, 41°, 46°, 52°, 61°, 71°, and 82° (2θ), which could not be assigned to any of the known ferrite or ferri/ferro (oxide)hydroxide phases and disappeared after CFO coating. This was also the case if the initial seeds were treated under coating conditions but in absence of any additional metal precursors, where reduction to Fe$_3$O$_4$ occurred. In this case, the seeds transformed into Fe$_3$O$_4$ nanorods exhibiting a similar structure to that of the Fe$_3$O$_4$/CFO nanorods but smaller dimensions (for TEM images, XRD analysis, and IR spectra of pure Fe$_3$O$_4$ nanorods as compared to seeds, see SI Figure S2). XRD patterns of the Fe$_3$O$_4$/CFO nanorods and the seeds (without baseline corrections) are displayed in Figure S1B. The increase in background with the Bragg angle (2θ) for Fe$_3$O$_4$/CFO nanorods is due to fluorescence of Co and further supports the formation of CFO. Broad reflections of low intensity in addition to very...
similar lattice parameters of Fe$_3$O$_4$ and Co$_{x}$Fe$_{3-x}$O$_4$ further prevent a detailed phase analysis by XRD. Any amorphous components, which may potentially form during CFO coating of the seeds, may also not be determined by XRD analysis. Therefore, Mössbauer, IR, and Raman spectroscopy as well as electron microscopy with elemental analysis (EDX) were additionally carried out to characterize the structure and composition of the CFO coated nanorods.

The IR spectrum of Fe$_3$O$_4$/CFO nanorods shows two protruding bands for the lattice vibration at 578 and 381 cm$^{-1}$ (Figure 2B). Since these bands can be assigned to both ferrites, i.e., Co ferrite (575 cm$^{-1}$/374 cm$^{-1}$) and Fe ferrite (570 cm$^{-1}$/370–380 cm$^{-1}$), it is not possible to clearly identify the ferrite phase of the Fe$_3$O$_4$/CFO nanorods using IR spectroscopy alone. However, complementary Raman analysis confirmed the presence of both ferrites (i.e., Fe$_3$O$_4$ and CoFe$_2$O$_4$) in the Fe$_3$O$_4$/CFO nanorods. The Raman spectrum reveals the four bands at 661, 382, 273, and 221 cm$^{-1}$ characteristic for Fe$_3$O$_4$ in addition to two bands at 624 and 467 cm$^{-1}$ characteristic for Co ferrite (Figure 2C), indicating both the reduction of the initial nanorod seeds to Fe$_3$O$_4$ and their successive coating with CFO.

**Electron Microscopy.** High resolution transmission electron microscopy (HRTEM), high angle annular dark field–scanning transmission electron microscopy (HAADF STEM), and SEM in combination with elemental analysis (EDX) were employed to further investigate the structure and spatial composition of the nanorods. Elemental maps of both the seeds and the Fe$_3$O$_4$/CFO nanorods by SEM EDX also show the overall presence of cobalt in the Fe$_3$O$_4$/CFO nanorods (Figure 3A and B). TEM and SEM images of the seeds and the Fe$_3$O$_4$/CFO nanorods are displayed in Figure 1. HRTEM images (Figure 3C) reveal the polycrystalline structure of the Fe$_3$O$_4$/CFO nanorods. The lattice fringes are clearly visible, indicating their overall good crystallinity. The lattice spacings are 2.99 and 2.56 Å, which is in good agreement with the (220) and (311) planes of a ferrite phase (either Fe$_3$O$_4$ or CoFe$_2$O$_4$), respectively. EDX line profile showing the distribution of Fe (green) and Co (blue) over the diameter of a single Fe$_3$O$_4$/CFO nanorod (inset, red line). Fe and Co distribution over the nanorod diameter indicates a Fe$_3$O$_4$ core/Co$_{x}$Fe$_{3-x}$O$_4$ shell structure of the nanorods (inset: high angle annular dark field STEM image (HAADF STEM) of Fe$_3$O$_4$/CFO nanorod).
Co$_3$Fe$_7$O$_{14}$ shell structure for the Fe$_3$O$_4$/CFO nanorods. This is also in good agreement with the results of Raman spectroscopy showing the presence of both Fe$_3$O$_4$ and CFO in the Fe$_3$O$_4$/CFO nanorods. The overall Co content of the rods based on the ICP OES analysis (Co/Fe = 1:3.9) seemed to be slightly increased as compared to the theoretical Co content of a 7.1 nm size Fe$_3$O$_4$/C.3 nm thick CFO shell structure, which could suggest some minor insertion of Co$^{3+}$ in the Fe$_3$O$_4$ core. Postsynthetic cation exchange of Fe$^{2+}$ to Co$^{2+}$ was previously reported for Fe$_3$O$_4$ nanocrystals.13

**Magnetic Properties.** It is well known that the reaction parameters, e.g. the ligand concentration and the ligand to particle ratio, affect not only the morphology but also the properties of core/shell nanoparticles.48,49 Therefore, the influence of the ligand on the particle morphology and $M_s$ was further investigated. While the reduction of the ligand concentration by half led to insoluble agglomerates, the doubling yielded nanorods, which were not only soluble in chloroform and n hexane but also showed a slightly increased $M_s$ at 293 K compared to the seeds. The ratio of oleic acid to oleylamine was also important: The nanorods behaved identically within the error of measurement in terms of morphology and $M_s$ when a ratio of >1 was employed, whereas those obtained with an oleic acid/oleylamine ratio of 1:2 showed a significant increase in $M_s$ (see Figure 4A). As determined by TGA measurements, 30 and 21 wt % organic ligands remained adsorbed on the seeds and the CFO coated particles after synthesis, respectively. Considering the organic residues on the MNP surface, the magnetization data were normalized to estimate the magnetization of the inorganic particle core.

In order to gain a deeper insight into the structure and magnetic behavior, the Fe$_3$O$_4$/CFO nanorods were characterized via field dependent magnetization curves, ZFC/FC curves, and Mössbauer spectroscopy. Fe$_3$O$_4$/CFO nanorods showed a broad magnetic hysteresis at 5 K with a coercive field of approximately 1.1 T, as is common for CFO nanoparticles, and a high field magnetization $M_{HF}$ of approximately 42 Am$^2$/kg (Figure 4B), considerably higher than that of the untreated seed material, shown for comparison. The large specific surface area and interface area of the Fe$_3$O$_4$/CFO nanorods (e.g., due to the polycrystalline and/or core/shell structure) may lead to considerable frustration of spins and further reduce the particles’ magnetization significantly compared to bulk CFO and magnetite. ZFC FC curves of the Fe$_3$O$_4$/CFO nanorods are shown in Figure 4C (black) together with the difference curve $m_{FC}-m_{ZFC}$ (red, solid line) and the differentiated difference curve (red, dotted line), often assumed to be indicative of the distribution of blocking temperatures $P(T_B)$ as described by50,51

$$P(T_B) \propto \frac{d(m_{FC} - m_{ZFC})}{dT}$$

The observed curves are characteristic for the transition from magnetically blocked to superparamagnetic behavior, with a $T_B$ of approximately 140 K, marked by the inflection point in the ZFC–FC difference magnetization curve.51 However, a minor splitting of FC and ZFC magnetization up to approximately 400 K indicates a small fraction of particles with higher $T_B$.

To get a better understanding of magnetic relaxation processes and the distribution of relaxation times, and to test the possibility of future experiments on nanorods in fluid media, the Fe$_3$O$_4$/CFO nanorods were dispersed in an organic carrier medium (i.e., Edwards L9) using LP4/KoratinSH (volume ratio 18/1/1) to yield a ferrofluid of 1.1 wt % ferrite nanoparticle concentration. A mapping of the imaginary part $\chi''$ of the magnetic AC susceptibility of the sample fluid was obtained via measurements with a high point density in frequency and temperature (Figure 5), as described in the

**Figure 5.** Color map of the imaginary part of AC magnetic susceptibility $\chi''$ (5–330 K, 10 K per step, and 0.1–1500 Hz, 8 steps per magnitude). The signal was interpolated between the experimental data points.

**Experimental Procedures.** As now spatial rotation of the particles is enabled in the fluid via Brownian particle motion, in addition to the Néel type relaxation of particle superspins, two major streak like features are visible, corresponding to the peaks in more common frequency dependent AC measurements, representing the relaxation time of magnetic moments in the system at hand at a defined temperature.52 While the
Fe\textsubscript{3}O\textsubscript{4}/CFO nanorods are completely magnetically blocked up to ca. 70 K, a broad distribution of different relaxation times is visible at higher temperatures. As the solution can be considered an amorphous solid until much higher temperatures, preventing any magnetic realignment via spatial particle rotation, this contribution can be assigned to Neél type relaxation of the particle magnetic moments. A maximum of this distribution is visible at approximately 140 K, matching the relaxation of the particle magnetic moments. A maximum of the magnetic moment via spatial particle rotation on the frequency scale of the AC susceptibility, the general agreement of $T_B$ observed in magnetization measurements of the nanoparticle powder and AC susceptibility of the dissolved nanoparticles indicates the absence of strong magnetic interparticle interaction, which would lead to a considerably increased blocking temperature for the powder sample. This could be explained by a diminished net magnetization, especially of the outer regions of the nanoparticles, caused by strong spin frustration (inferred from in-field Mössbauer spectroscopy discussed in the following section) likely to be located at internal interfaces, as well as at the particle surface, as the somewhat irregular surface geometry may result in an enhanced specific surface area of the particles.

In Figure 5, an additional streak appears at approximately 250 K, representing the realignment of the particle magnetic moments via spatial particle rotation on the frequency scale of our experiments, as the solution reaches sufficiently low viscosities. Particles, which are still magnetically blocked in terms of Neél relaxation, now also display a quasi superparamagnetic behavior: blocking temperatures studied in AC susceptibility measurements of the nanoparticle powder and AC susceptibility of the dissolved nanoparticles indicates the absence of strong magnetic interparticle interaction, which would lead to a considerably increased blocking temperature for the powder sample. This could be explained by a diminished net magnetization, especially of the outer regions of the nanoparticles, caused by strong spin frustration (inferred from in-field Mössbauer spectroscopy discussed in the following section) likely to be located at internal interfaces, as well as at the particle surface, as the somewhat irregular surface geometry may result in an enhanced specific surface area of the particles.

Mössbauer Spectroscopy. Complementary Mössbauer experiments were performed to analyze the magnetic structure of the particles’ individual components and their magnetic alignment behavior. Mössbauer spectra of the nanoparticle powder (Figure 6) as well as the seed crystals (Figure S3) were recorded at temperatures down to 4.3 K. In the case of untreated seed crystals, the presence of Fe\textsuperscript{3+} and Fe\textsuperscript{2+} states in Mössbauer spectra show a transition to an ordered sextet structure at similar temperatures of ca. 30–40 K, which could indicate a Fe hydroxide-carbonate phase (e.g., partially oxidized green rust (Fe\textsubscript{6−x}\textsuperscript{3+}Fe\textsubscript{x}\textsuperscript{2+}O\textsubscript{1+x}(OH)\textsubscript{x−1}(CO\textsubscript{3})\textsubscript{2}3H\textsubscript{2}O)\textsuperscript{42} or siderite (FeCO\textsubscript{3}), both showing matching ordering temperatures,\textsuperscript{53} possibly in a mixture with Fe\textsuperscript{3+} bearing six line ferrhydrite. CO\textsubscript{3}\textsuperscript{2−} may form during seed synthesis from Fe(CO\textsubscript{3})\textsubscript{2} under solvothermal conditions. However, a clear assignment to either of these Fe hydroxide-carbonate phases was not possible based on the IR spectra.

Mössbauer spectra of the Fe\textsubscript{3}O\textsubscript{4}/CFO nanopowder, on the other hand, display superparamagnetic properties: Upon rising temperature, a significant superparamagnetic contribution is visible, containing about 30% of spectral area (olive) at room temperature. The remaining fraction of magnetically blocked CFO and Fe\textsubscript{3}O\textsubscript{4} displays a sextet subspectrum with broad inner shoulders (violet), caused by beginning super paramagnetic relaxation, preventing the resolution of individual contributions of spinel tetrahedral A and octahedral B sites at elevated temperatures. The apparent contradiction to blocking temperatures as determined in magnetometry and suscep...
nanorod surface even at very limited thermal energy. These effects also prevent the possible detection of a minor Fe$^{3+}$ sextet subspectrum, whose presence would be expected assuming ca. 50 wt % Fe$_3$O$_4$ core material. Also, a partial oxidation of the nanorod core from magnetite to maghemite (γ Fe$_2$O$_3$) could further lead to a reduced Fe$^{2+}$ content in the particles.

The in field spectrum (Figure 6 top) shows partial splitting between A and B site subspectra, resulting from the different sublattice spin orientations relative to the external magnetic field, as expected for the ferrimagnetic CFO and Fe$_3$O$_4$ spinel phases. However, even in an external magnetic field of 5 T (aligned parallel to the γ ray propagation direction), the sample material displays considerable spin canting, close to a state of random spin orientation, visible via the relatively high intensity of lines no. 2 and 5 in the spectrum, from which an average spin canting angle of ca. 45° relative to the field direction can be inferred. Absorption lines in the in field spectrum are broadened and asymmetric to a certain degree, presumably caused by the superposition of slightly different CFO and Fe$_3$O$_4$ subspectral contributions and/or a minor magnetite Fe$^{2+}$ fraction, accounted for by the use of hyperfine field sextet distributions. The observation of considerable canting at 5 T matches the slow rise in field dependent magnetization, as discussed in the previous section, indeed pointing toward a locally highly frustrated spin structure rather than to a pronounced decrease in $M_r$ by antiferromagnetic or paramagnetic byproducts, which would be clearly visible in the in field Mössbauer spectrum when present in relevant concentrations. Thereby, we would connect the clearly visible signs of spin frustration to contributions of the iron oxide to cobalt ferrite interface, as well as of the undercoordinated surface atoms, as the nanorods’ specific surface area may be increased to some degree by the rough surface structure observable for some of the particles in TEM images (Figure 1). Frustrated spin structures may additionally be more likely even within the nanoparticles’ core due to the possible presence of structural defects arising from the phase transition of the original seed material to magnetite. The primary origin of spin frustration will be clarified in future investigations by comparing the spin structure of core-shell nanorods of different shell thickness.

CONCLUSION

For the first time, well defined, Fe$_3$O$_4$/CFO nanorods were prepared by a seed mediated synthesis with dimensions in the range of 1–100 nm. The Fe$_3$O$_4$/CFO nanorods revealed a mean length and width of 51.2 and 9.5 nm, respectively, corresponding to an aspect ratio of 5.4:1. The nanorods were colloidally stabilized in common organic solvents, which is an important aspect for future technical application. The formation of the Fe$_3$O$_4$/CFO nanorods was accompanied by a significant increase in $M_r$—as compared to the original nanorod seeds. ZFC/FC magnetization curves and a detailed AC susceptibility mapping display partial superparamagnetic behavior with an average $T_N$ of ca. 140 K and a broad distribution of Néel relaxation times. A maximum high field magnetization of 42 Am$^{-2}$/kg was determined by magnetometry at 4.3 K and 9 T. In field Mössbauer experiments demonstrated strong spin frustration in external fields of 5 T, probably located at the CFO surface or the Fe$_3$O$_4$/CFO interface, which is assumed to be the primary origin of limited high field magnetization. Further Mössbauer spectroscopy studies confirmed the expected magnetic spinel structure and blocking temperatures determined via magnetometry and allowed estimation of the amount of an Fe$^{3+}$ containing phase to approximately 10%. Future studies will be directed toward optimization of the CFO shell thickness and homogeneity in order to tune spin frustration effects. Overall, Fe$_3$O$_4$/CFO nanorods, investigated in this study, may provide ferrofluids in organic and aqueous carrier media with interesting magnetorheological properties, an aspect which will be another subject of future investigations.

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Notes

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