Supporting Information for: *In Situ* Powder X-ray Diffraction Study of Magnetic CoFe₂O₄ Nanocrystallite Synthesis

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Magnetic Nanoparticles

Figure 1S illustrates the size dependence of magnetic coercivity of hard magnetic nanocrystallites. For larger crystallites the material divides into magnetic domains of different orientations in order to minimize the magnetostatic energy. At the critical magnetic single-domain crystallite diameter, D_{sd} , the highest possible coercivity is achieved. Reducing the size further causes the particles to enter their superparamagnetic state in which constant flipping of the magnetic moments takes place. Consequently, by tuning the size of $CoFe_2O_4$ nanocrystallites the magnetic properties can be controlled and functional materials for specific applications may be tailored.



Figure 1S: Size dependence of the coercivity of hard magnetic materials. Larger crystallites divide into magnetic domains separated by domains walls, which lowers the coercivity of the materials. However, small single-domain nanocrystallites below the superparamagnetic limit constantly flip their direction of magnetization. The highest possible coercivity is achieved at the critical magnetic single-domain size (D_{sd}).

The critical magnetic single-domain crystallite diameter, D_{sd} , depends on several material specific properties. Furthermore, D_{sd} is strongly geometry-dependent.¹ For spherical magnets D_{sd} is given by $D_{sd}=[72(AK_1)^{1/2}]/(\mu_0 M_s^2)$, where A is the exchange constant, K_1 is the effective uniaxial magnetic

anisotropy constant, μ_0 is the vacuum permeability and M_s is the intrinsic spontaneous magnetization of the material.² For most magnetic materials D_{sd} is in the range of 10-100 nm, but for very hard magnets of high anisotropy D_{sd} may exceed 1 µm.

Precursor Preparation

The steps followed in the preparation of precursors for the temperature and [OH⁻] concentration series are shown in Table 1S. The precursor species were added in the given numeric order. The mixtures were thoroughly mixed in between each step in order to ensure a homogenous precursor. Upon addition of NaOH a gel formed, which was homogenized by vigorous mechanical mixing.

Table 1S: Preparation routes of the different precursors used in the investigation of the effect of synthesis temperature and precursor [OH⁻] concentration.

CFO_170C, CFO_270C	CFO_OH_1.5	CFO_OH_2.0	
(CFO_OH_1.25), CFO_320C,			
CFO_370C			
1) 2.0 ml 2.0 M Fe(NO ₃) ₃	1) 2.0 ml 2.0M Fe(NO ₃) ₃	1) 2.0 ml 2.0 M Fe(NO ₃) ₃	
2) 1.0 ml 2.0 M Co(NO ₃) ₂	2) 1.0 ml 2.0 M Co(NO ₃) ₂	2) 1.0 ml 2.0 M Co(NO ₃) ₂	
3) 1.25 ml 16.0 M NaOH	3) 1.5 ml 16.0 M NaOH	3) 2.0 ml 16.0 M NaOH	
4) 0.75 ml H_2O	4) 0.5 ml H_20		
NO ₃ ⁻ to NaOH ratio = 1:1.25	NO_3^- to NaOH ratio = 1:1.5 NO_3^- to NaOH ratio = 1:2.0		

The steps shown in Table 2S were followed in the preparation of precursors with different metal ion concentration upon NaOH addition. Again, the precursor species were added in the given numeric order. In this series of experiments a less concentrated NaOH solution of 12 M was used in the precursor preparation. An amount of NaOH corresponding to 1.0 times the molar amount of NO_3^- ions in the solution was added. As was the case in the first series of experiments, a gel formed when the base was added for all three precursors.

Table 2S: Preparation routes of the three different precursors used in the investigation of the effect of metal ion concentration when adding the base.

CFO_M_2.0	CFO_M_1.0	CFO_M_0.5	
1) 1.5 ml 2.0 M Fe(NO ₃) ₃	1) 1.5 ml 2.0 M Fe(NO ₃) ₃	1) 1. 5 ml 2.0 M Fe(NO ₃) ₃	
2) 0.75 ml 2.0 M Co(NO ₃) ₂	2) 0.75 ml 2.0 M Co(NO ₃) ₂	2) 0.75 ml 2.0 M Co(NO ₃) ₂	
3) 1.0 ml 12.0 M NaOH	3) 2.25 ml H20	3) 6.75 ml H_2O	
4) 6.75 ml H_2O	4) 1.0 ml 12.0 M NaOH	4) 1.0 ml 12.0 M NaOH	
	5) 4.5 ml H2O		
Metal ion concentration upon	Metal ion concentration upon	Metal ion concentration upon upon	
addition of base = 2.0 M	addition of base = 1.0 M	addition of base = 0.5 M	

Temperature Profiles

Representative temperature profiles for the *in situ* setup measured by inserting a thermocouple in a water filled capillary are shown in Figure 2S.



Figure 2S: Temperature profiles of the *in situ* PXRD setup for various set temperatures.

The set temperature T_s is given along with the equilibrium temperature T_{180s} measured after 180 s. The rapid heating by the hot air jet is obvious as the actual temperature in the capillary is generally within 10% of the set temperature after only 20 s.

In Situ Powder X-ray Diffraction Setup

The working principle of the *in situ* PXRD setup is illustrated in Figure 3.



Figure 3: Illustration of the in situ PXRD experimental setup.

The capillary containing the precursor solution is pressurized with demineralized water and heated by a jet of hot air. As the nanocrystallites form, the monochromatized synchrotron X-ray beam diffracts from the sample and the resulting diffraction pattern is collected on a 2D area detector. The crystallization is followed *in situ* with a time resolution of 5 seconds by sequentially reading out the detector.

In Situ Powder X-ray Diffraction Data

Examples of raw *in situ* PXRD data frames are shown in Figure 4S. The bright dots stem from the single crystal sapphire capillary which was used as a reaction vessel. Furthermore, a small part of the detector (lower right corner) was covered by oil spots. The oil spots and single crystal peaks were masked in the *Fit2D* software prior to integration and further analysis.³



Figure 4S: (A) Raw PXRD data frame of sample CFO_270C prior to heating. (B) Raw PXRD data frame of sample CFO_270C obtained after 5 minutes of hydrothermal treatment at 250 bar and 270 °C. (C) Example of NIST LaB_6 standard sample data.

By integrating the data and cascading the diffraction patterns the phase evolution can be illustrated in a contour plot as shown in Figure 5S.



Figure 5S: Contour plot if *in situ* data from hydrothermal treatment of CFO_270C at 270 °C and 250 bar.

The Fit2D software was used to calculate the sample to detector distance and accurately determine the synchrotron wavelength at each individual beamtime using data measured on a NIST LaB₆ calibrant. At the first beamtime the wavelength was found to be 1.0011 Å and the sample to detector distance was 89.35 mm. At the second beamtime the wavelength was 0.9941 Å and the sample to detector distance was 89.71 mm.

Sequential Rietveld Refinement

The obtained diffraction patterns were analysed by sequential Rietveld refinement using the *Fullprof Suite* software package.⁴ The refinements of the cobalt ferrites were done based on the structure of $CoFe_2O_4$ in the cubic *Fd*-3*m* space group. The tetrahedral and octahedral sites were assumed to be fully occupied, with 2/3 Fe³⁺ and 1/3 Co²⁺. The site occupancies were fixed at these values throughout the sequential refinements. The background was modelled by a linear interpolation between a set of background points with refinable intensity. The Thompson-Cox-Hasting numerical approximation of the pseudo-Voigt function was used in the modelling of the peak profiles. The zero-point shift was refined for the last frame in the given series and kept fixed at the resulting value in the sequential refinement. The thermal parameters, occupancy and atomic positions were held fixed in the refinements. The scale factor, unit cell parameter (*a*), peak profile parameters related to size (Lorentzian (*Y*) and Gaussian (*I_G*) contribution) and background were all refined.

The average volume-weighted sizes of the coherently scattering crystalline domains $\langle D \rangle$ were calculated from the Scherrer formula, $FWHM = (K \cdot \lambda)/(\langle D \rangle \cdot \cos(\theta))$. Here, λ is the X-ray wavelength and θ is the Bragg angle. A shape factor K of 0.94 was used, assuming isotropic crystallite morphology.⁵ The full width half max FWHM was calculated from the refined Y and I_G values. The provided uncertainties on the crystallite sizes are extrapolated from the standard deviations of the fitted peak profile parameters related to size. However, considering the absolute error on the experiment, the uncertainty is significantly larger.

Phase Investigation

The unit cell parameters of the hexagonal α -Fe2O3 phase obtained in the phase investigation experiment were refined to a=5.076(1) Å and c=13.858(1) Å.

TEM Considerations

The TEM measurements were done *ex situ* at room temperature and the sample may have been the subject of post synthesis modifications due to the cooling, TEM sample preparation, etc. Due to the inhomogeneous heating of the reactor, care must be taken when comparing sizes from PXRD data collected from the center of the capillary with TEM sizes from images of material collected from the entire hot-zone of the capillary. Furthermore, when collecting the sample from the capillary an amount of unreacted precursor is inevitably flushed out along with the product. In addition, in TEM micrographs only a very small part of the sample is represented as opposed to PXRD where the whole sample volume is probed. TEM size analysis gives the number weighted sizes of the entire particles which may consist of multiple crystallites, amorphous layers, etc., while Scherrer analysis yields volume weighted sizes of coherently scattering crystalline domains. Consequently, comparison of absolute sizes from the two techniques is not straightforward and should be done with care.

Hysteresis Measurement and Analysis

The field dependent magnetization curves were measured by cycling the external field from+20 to -20 kOe at 300 K. Only very small amounts of $CoFe_2O_4$ ($m_{CFO powder}$) were available for the hysteresis measurements (see Table 3S). Therefore, the material was mixed with graphite powder (ChemPUR, >99%) in order to have enough material for compaction into 2.5 mm diameter pellets. The compaction prevents physical movement of the particles during the experiments. The sample powders were thoroughly mixed with a known amount of graphite ($m_{Graphite powder}$) and the amounts of $CoFe_2O_4$ (m_{CFO}_{pellet}) and graphite ($m_{Graphite pellet}$) in the final pellets was determined from the pellet mass (m_{Pellet}) and the powder mass ratio ($m_{CFO powder}/m_{Graphite powder}$).

Sample:	m _{CFO powder}	m _{Graphite}	<i>m</i> _{CFO powder} /	m _{Pellet}	m _{CFO pellet}	$m_{ m Graphite\ pellet}$
		powder	M Graphite powder			
CFO_M_0.5	1.79 mg	7.74 mg	0.232	3.96 mg	0.92 mg	3.04 mg
CFO_M_1.0	0.45 mg	6.89 mg	0.066	3.00 mg	0.20 mg	2.80 mg
CFO_M_2.0	1.11 mg	7.47 mg	0.148	3.95 mg	0.59 mg	3.37 mg

Table 3S: Amounts of $CoFe_2O_4$ and graphite powder used in the preparation of the pellets. The masses were measured on a Mettler AT20 balance with an uncertainty of $5*10^{-3}$ mg.

The measured sample hysteresis curves are shown in Figure 6S (A). The graphite contribution was determined by measurement of a pure graphite pellet ($m_{\text{Reference}}$ =11.506 mg) under equivalent conditions. The graphite reference measurement with corresponding linear fit used for the graphite correction is shown in Figure 6S (B).



Figure 6S: (A) Field dependent magnetization curves of the three samples prior to graphite correction and mass normalization. (B) Field dependent magnetization curve of the graphite reference with linear fit. The fitted values are shown in the bottom left corner.

The actual CoFe₂O₄ magnetization curves (M_{CFO}) were found by subtracting the contribution of the graphite ($M_{Graphite}$) from the measured data ($M_{Measured}$).

$M_{\rm CFO} = M_{\rm Measured} - M_{\rm Graphite}$

The field dependent contribution from the graphite was calculated and corrected for using the linear fit to the reference measurement, divided by $m_{\text{Reference}}$ and multiplied by the graphite mass in the given sample ($m_{\text{Graphite pellet}}$).

$$M_{\text{Graphite}} = (M_{\text{Reference}}/m_{\text{Reference}})^* m_{\text{Graphite pellet}}$$

Finally, the mass weighted magnetic hysteresis for the $CoFe_2O_4$ nanoparticles ($M_{CFO mw}$) was determined as follows.

 $M_{\rm CFO\ mw} = M_{\rm CFO}/m_{\rm CFO\ pellet}$

The reported coercivities and remanences were estimated from linear fits to the 10 data points closest to the actual values, i.e. crossings of X and Y axes, in the mass weighted hysteresis curves. Uncertainties on the values were estimated by propagation of error from the standard deviations of the fit.

References

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