Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2013

Supporting Information

Size dependent structural and magnetic properties of FeO/Fe_3O_4 nanoparticles

Aidin Lak,[a] Mathias Kraken,[b] Frank Ludwig,[a] Andreas Kornowski,[c] Dietmar Eberbeck,[d] Sibylle Sievers,[e] F. J. Litterst,[b] Horst Weller,[c] and Meinhard Schilling[a]

[a] Institute of Electrical Measurement and Fundamental Electrical Engineering, TU Braunschweig, Hans-Sommer-St. 66, 38106 Braunschweig, Germany.

[b] Institute of Condensed Matter Physics, TU Braunschweig, Mendelssohn-St. 3, 38106 Braunschweig, Germany.

[c] Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany.

[d] Physikalisch-Technische Bundesanstalt, Abbe-St. 2-12, 10587 Berlin, Germany.

[e] Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany.

Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2013

1 Experimental Procedure

1.1 Materials

$FeCl_3.6H_2O$ (98%), 1-octadecene (ODE, 90%), tetracosane (TC, 90%), docosane (DC, 90%), hexane (95%), ethanol (99.8%), chloroform (99.9%) and gypsum were purchased from Sigma-Aldrich. Oleic acid (99%) and sodium oleate (97%) were purchased from TCI. All the chemicals were utilized "as received" and without further purification.

1.2 Synthesis of nanoparticles

All the particles were synthesized using a freshly obtained iron(III)-oleate precursor (recipe can be found in [1]) to skip the impact of aging and oxidation of the precursor on particle size distribution and composition.

In a typical synthesis of 18 nm particles, 2 mmol iron-oleate, 6 mmol oleic acid and 10 mL solvent (2:1 w/w, ODE:TC)) were poured into a glass flask attached to a Schlenk line. Afterwards, the mixture was degassed and dried at 100°C for 10 min through a frequent evacuation and filling with argon. This step was carried out to eliminate any remaining traces of volatile impurities and water. The resultant reddish transparent liquid was heated up to 337°C at a heating rate of 3°C/min and let to reflux for 60 min under flow of argon. The obtained black suspension was cooled to 60°C, washed by adding a 3:1 acetone/hexane mixture and then the particles were separated by centrifuging. This process was repeated three times to remove impurities. Finally, the particles were dispersed in chloroform/toluene. To avoid undesirable effect of aging/oxidation on the particle properties, characterization experiments were carried out within one week after washing and dispersion of the particles. The 13 and 24 nm particles were synthesized by reducing the growth time to 30 min and increasing the growth temperature to 357°C, respectively, while the other parameters remained unchanged.

Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2013

2 Characterization

2.1 Structural analysis

High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) studies were carried out utilizing a double spherical aberration corrected field emission microscope (JEOL, 200 keV). The samples were prepared by drying a drop of highly clean and diluted particle suspensions on carbon coated TEM copper grids. The X-ray diffraction (XRD) technique was employed to identify the particle crystal structure, distinguish different iron oxide phases and determine the particle average crystallite size. The XRD patterns are taken on dried samples utilizing a PANalytical X'Pert PRO machine using Cu K_α X-ray source.

To quantitatively determine the particle phase composition, Mössbauer absorption measurements were performed using a conventional Mössbauer spectrometer with a ^{57}CoRh source kept at room temperature. The absorber temperature can be varied from 4 K to 300 K using a LakeShore 336 temperature controller. The Mössbauer samples were prepared by drying freshly synthesized particles under high vacuum. The samples were stored in an air-free atmosphere until measured.

2.2 Magnetic characterization

Magnetic measurements were carried out on both mobile (i.e. particle suspensions in toluene) and immobile samples using a magnetic property measurement system (MPMS-XL, Quantum Design). The immobile samples were prepared by solidification of 87 μL of particle suspension with 87 mg of gypsum in polycarbonate capsules. Temperature dependent magnetization measurements were performed on the immobile samples in an external DC magnetic field of 1 mT. Field cooled (FC) $M-H$ magnetization curves were recorded after the samples were cooled from room temperature to a temperature below the Néel temperature T_N of FeO in a cooling field of 5 T. Zero field cooled (ZFC) $M-H$ hysteresis loops were acquired by setting a nominal field of -0.03 mT to compensate the residual magnetic field of the system. All the presented magnetization data are corrected with respect to the diamagnetic and paramagnetic effects of gypsum.

This journal is © The Royal Society of Chemistry 2013

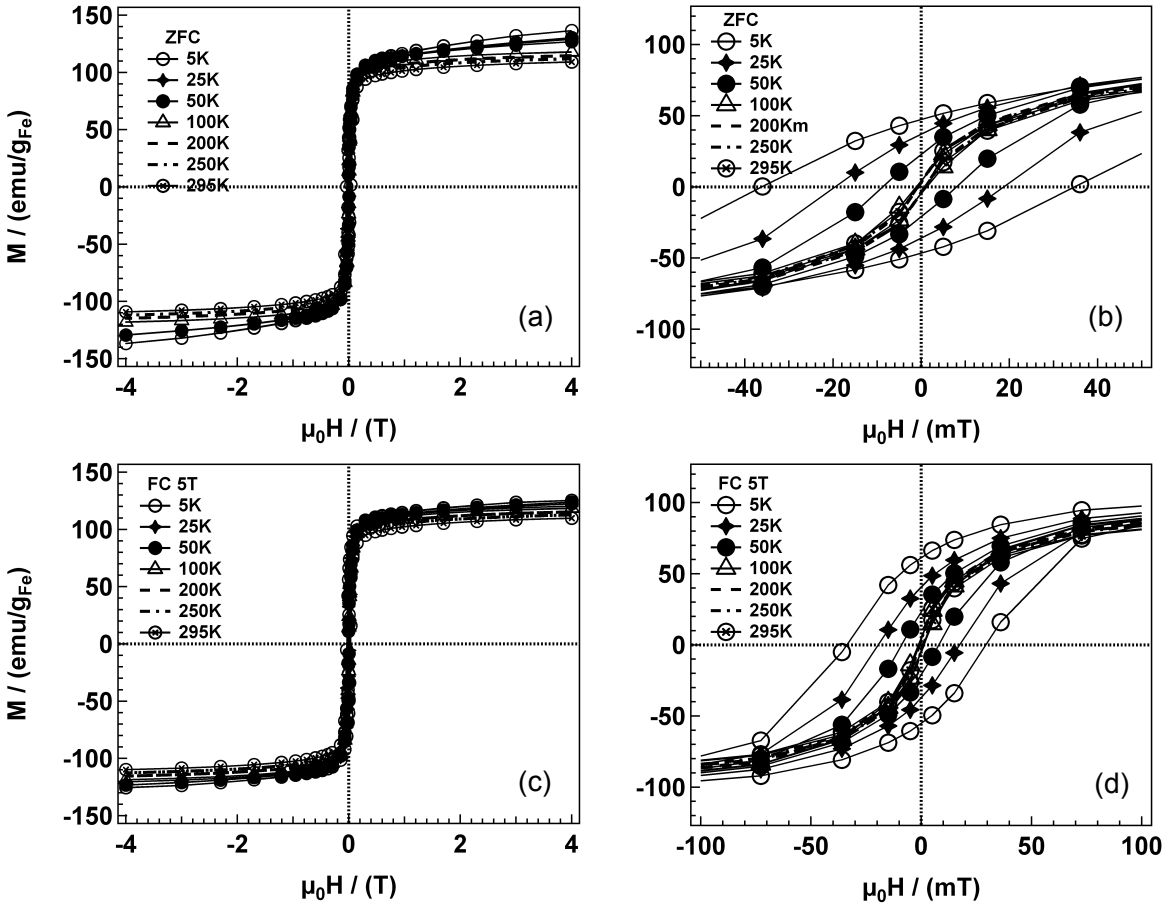

Fig. S 1: (a), (b) ZFC and (c), (d) FC magnetizations of 13 nm Fe_3O_4 NPs versus magnetic field in the cooling field of 5 T taken at different temperatures.

This journal is © The Royal Society of Chemistry 2013

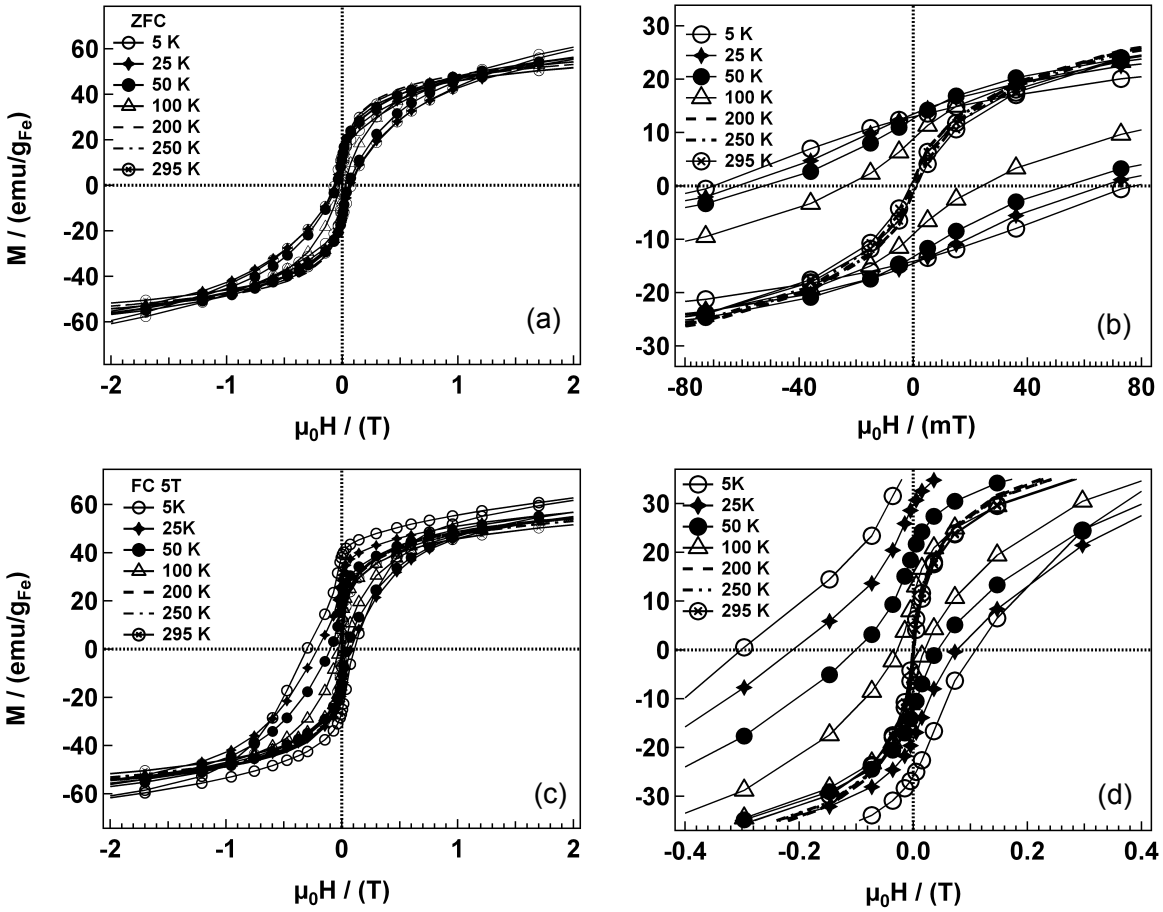

Fig. S 2: (a), (b) ZFC and (c), (d) FC magnetizations of 18 nm FeO/Fe_3O_4 NPs versus magnetic field in the cooling field of 5 T taken at different temperatures.

This journal is © The Royal Society of Chemistry 2013

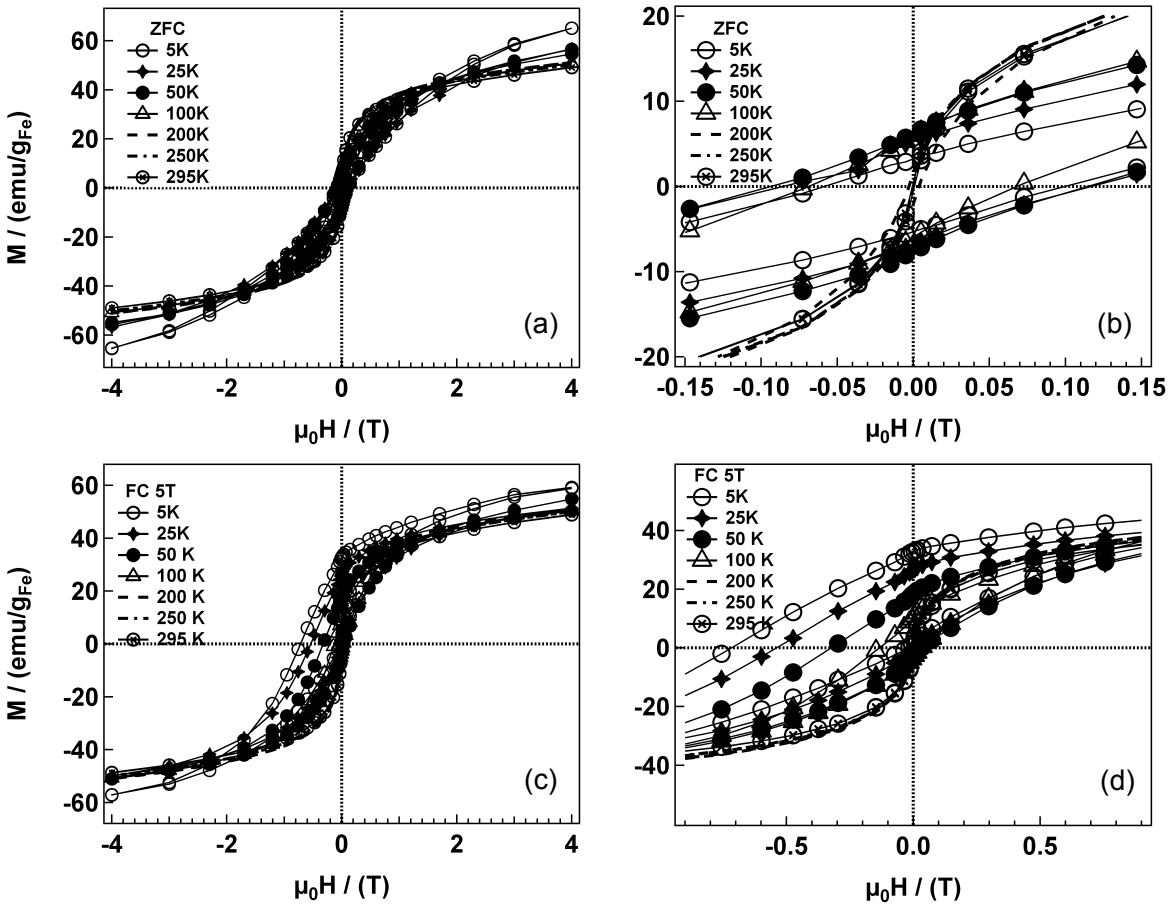

Fig. S 3: (a), (b) ZFC and (c), (d) FC magnetizations of 24 nm FeO/Fe_3O_4 NPs versus magnetic field in the cooling field of 5 T taken at different temperatures.

Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2013

References

[1] A. Lak, F. Ludwig, J. M. Scholtyssek, J. Dieckhoff, K. Fiege, and M. Schilling. Size distribution and magnetization optimization of single-core iron oxide nanoparticles by exploiting design of experiment methodology. *IEEE Trans. Magn.*, 49:201–209, 2013.