Supporting Information

Self-assembly of smallest magnetic particles

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Sample Preparation and Overview

The nanoparticles were synthesized via thermal decomposition of iron(III)-oleate in the presence of the stabilizing ligand oleic acid. Iron(III)-oleate was prepared from stoichiometric molar ratios of sodium-oleate and iron(III)-chloride (3:1) or with an excess of sodium-oleate (3.09:1, 3.15:1, 3.30:1). With small excess of sodium-oleate spherically shaped nanoparticles are obtained, whereas a larger excess leads to the formation of very regular cube-shaped nanoparticles. The exact synthesis protocols for spherically and cube-shaped nanoparticles of given diameter are summarized in Table S1.

shape	diameter [nm]	Na/Fe-ratio in oleate	heating rate [°C/min]	growth temperature [°C]	growth time [min.]
sphere	4-6	3.09 : 1	2.0	317	8-10
sphere	7-12	3.09 : 1	3.3	317	10
sphere	13-20	3.00 : 1	3.3	320	15
cube	4-6	3.09 : 1	2.0	317	8-10
cube	7-8	3.15 : 1	2.0	317	15
cube	9-10	3.30 : 1	2.0	317	20

Table S1: Synthesis protocols for the synthesis of spherical and cube-shaped nanoparticles of different size.

The nanoparticles were worked-up and purified by precipitation and centrifugation in acetone to remove remaining oleate precursor and excess oleic acid. The nanoparticles were dried, redispersed in toluene, and stored under reduced temperature. The use of magnetic stirring devices was avoided during synthesis to keep the nanoparticles in their non-aggregated, singly dispersed state.

Sample	**shape**	**magnetic 3D assemblies**	**diameter/edge length**
G116	cubic	yes	9 nm
G25	cubic	yes	8.2 nm
G102	cubic	yes	7.5 nm
G85	cubic	no	6.5 nm
G73	spherical	no	14.8 nm
G43	spherical	no	13.3 nm

Table S2: Overview over the investigated iron oxide samples. The diameters correspond to the pure iron oxide nanoparticles. They are stabilized by an oleic acid layer of ca. 2 nm.

TEM of iron oxide nanoparticle

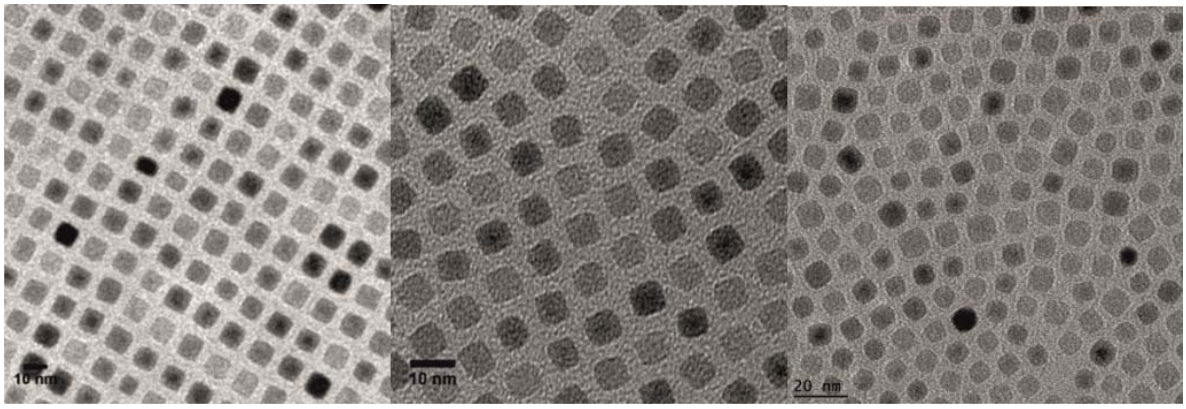

Fig. S1: TEM-images of cube-shaped nanoparticles, left: G25, middle: G85, right: G102. Samples G25 and G85 have a very regular cubic shape with only small edge truncations. Sample G102 has larger truncations.

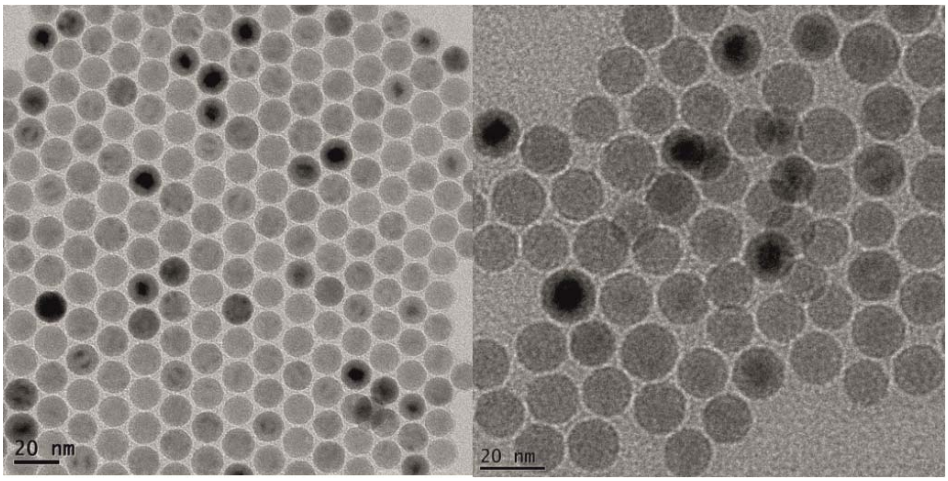

Fig. S2: TEM-images of spherically-shaped nanoparticles, left: G43, right: G73. The samples have very regular spherical shape and narrow size distributions.

Cryo-electron microscopy images of cubic nanoparticles

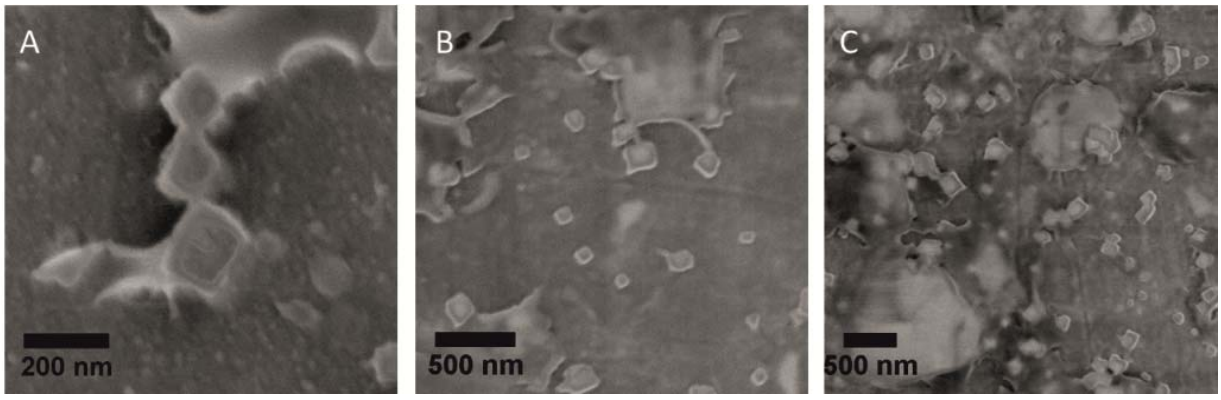

Fig S3. **A-C.** Cryo-SEM images of three-dimensional cuboids of G25 iron oxide nanoparticles in toluene. The cuboids are formed in the presence of an external magnetic field.

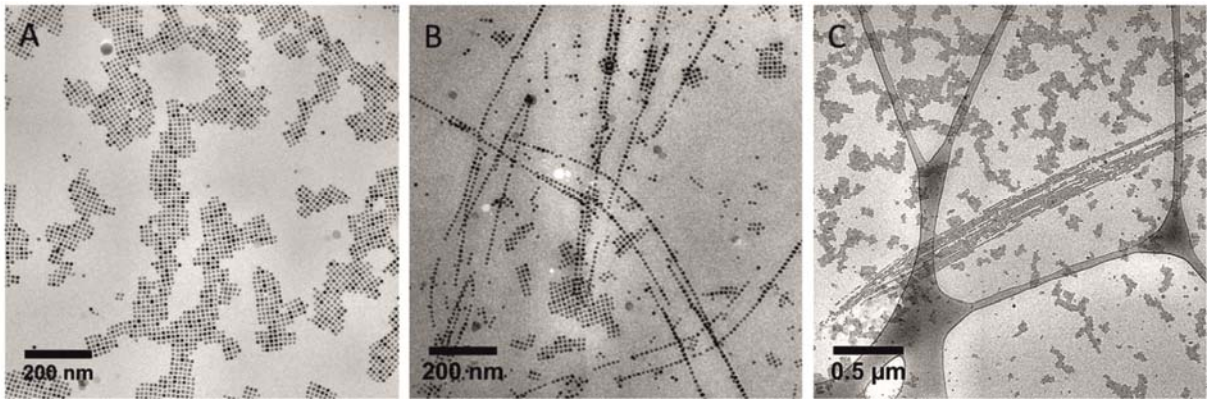

Fig S4. Cryo-TEM images of G25 iron oxide nanoparticles coated with oleic acid in toluene. The data were obtained after exposing the sample to a magnetic field of 130 mT at 253 K and show **A**. aggregated sheets, **B**. and **C**. long chains, ribbons and sheets.

Orientation of the magnetization assuming freely adjustable dipoles

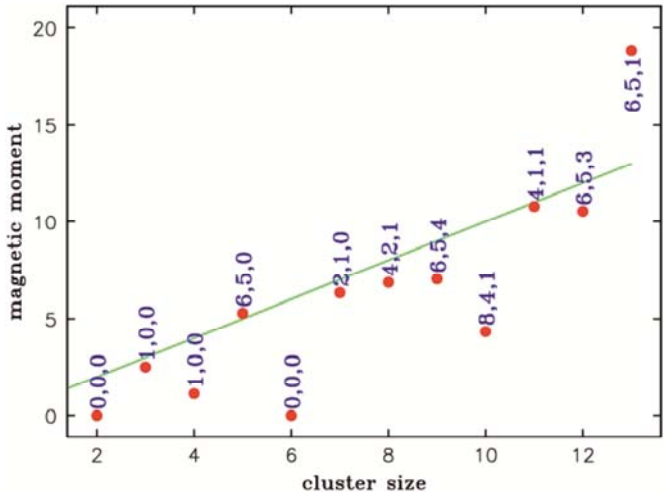

Fig S5. Preferred orientation of the magnetization within cubic superlattices. A cluster of size N corresponds to N^3 nanoparticles arranged in a cubic lattice.

Assembly of spherical shaped nanoparticles

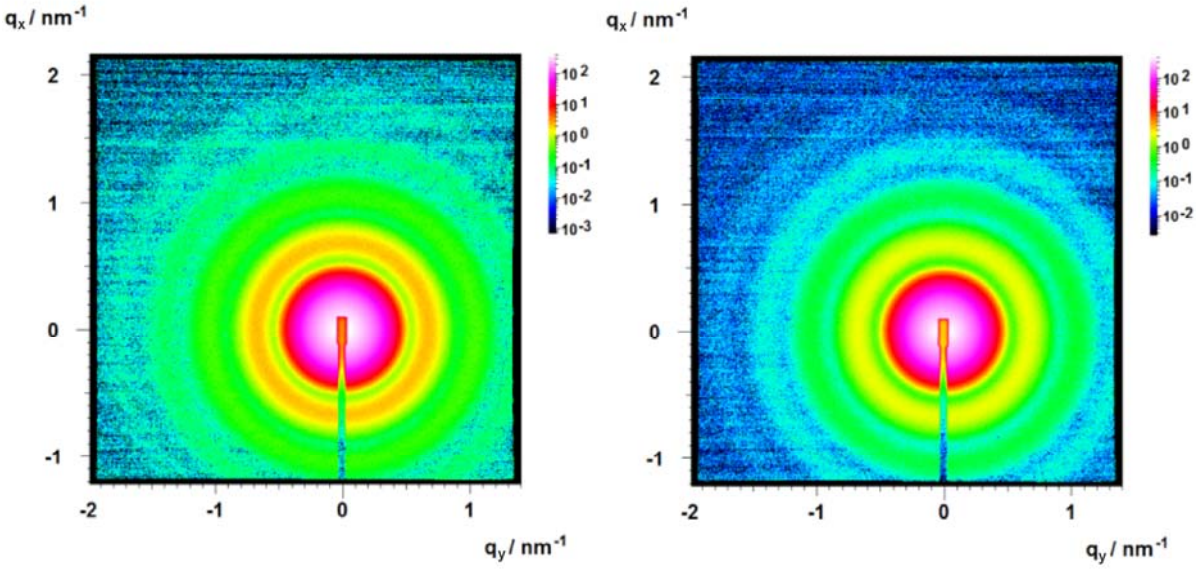

Fig. S6 Synchrotron SAXS-patterns measured for spherical G73 nanoparticles at a concentration of 18 wt% in toluene at 0.0 T (left) and 0.98 T (right). The scattering patterns just show form factor oscillations. There is no indication of ordered clustering.

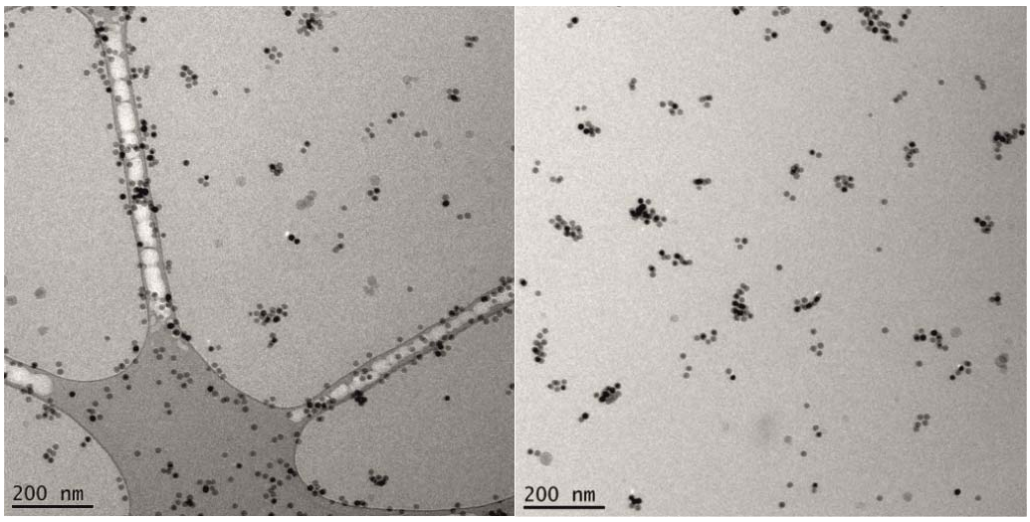

Fig. S7 Cryo-TEM of spherical iron oxide nanoparticles (G43) after exposure to an external magnetic field of 130 mT. The nanoparticles show some aggregation into clusters. An arrangement into geometrically well-defined, ordered assemblies is not observed.

SAXS of cube-shaped nanoparticle assemblies

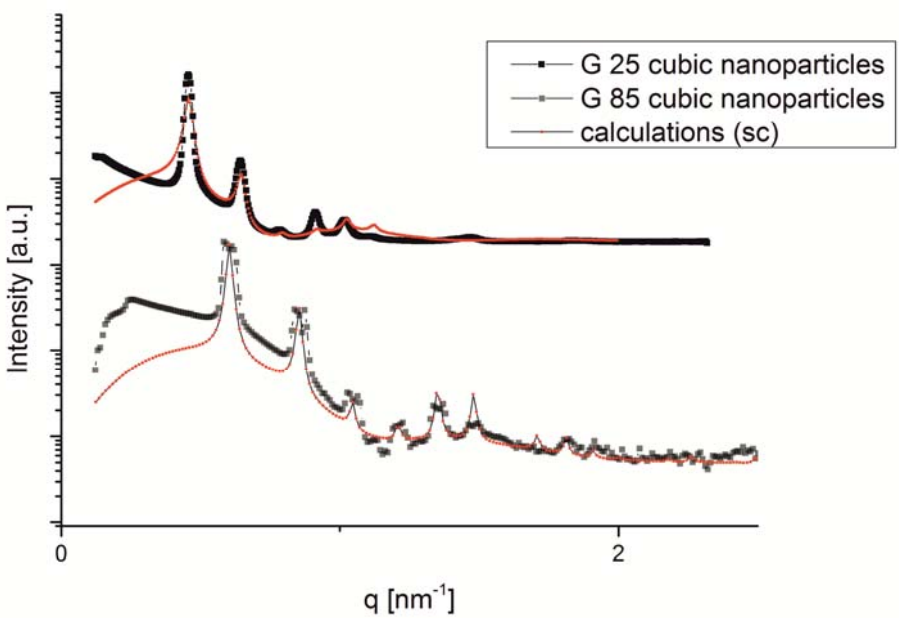

Fig. S8: SAXS curves measured for the cubic nanoparticles G25 and G85 in the dry state. Red lines are fits to a simple cubic (Pn3m) lattice.

FC- and ZFCM measurements of magnetic nanoparticles

The magnetization data were collected using a MPMSXL-5 SQUID magnetometer under an applied field of 50 Oe over the temperature range 2 to 300 K in the settle mode (FCM/ZFCM). For the zero field cooled magnetization measurements, the magnetic field was set to zero at room temperature and the sample was cooled down to 5 K before the magnetic field was switched on. For the hysteresis loops the magnetic field was varied between +/- 1 T. The dried samples were placed in gelatine capsules held within a plastic straw. The solution was measured in a sealed quarz glass tube.

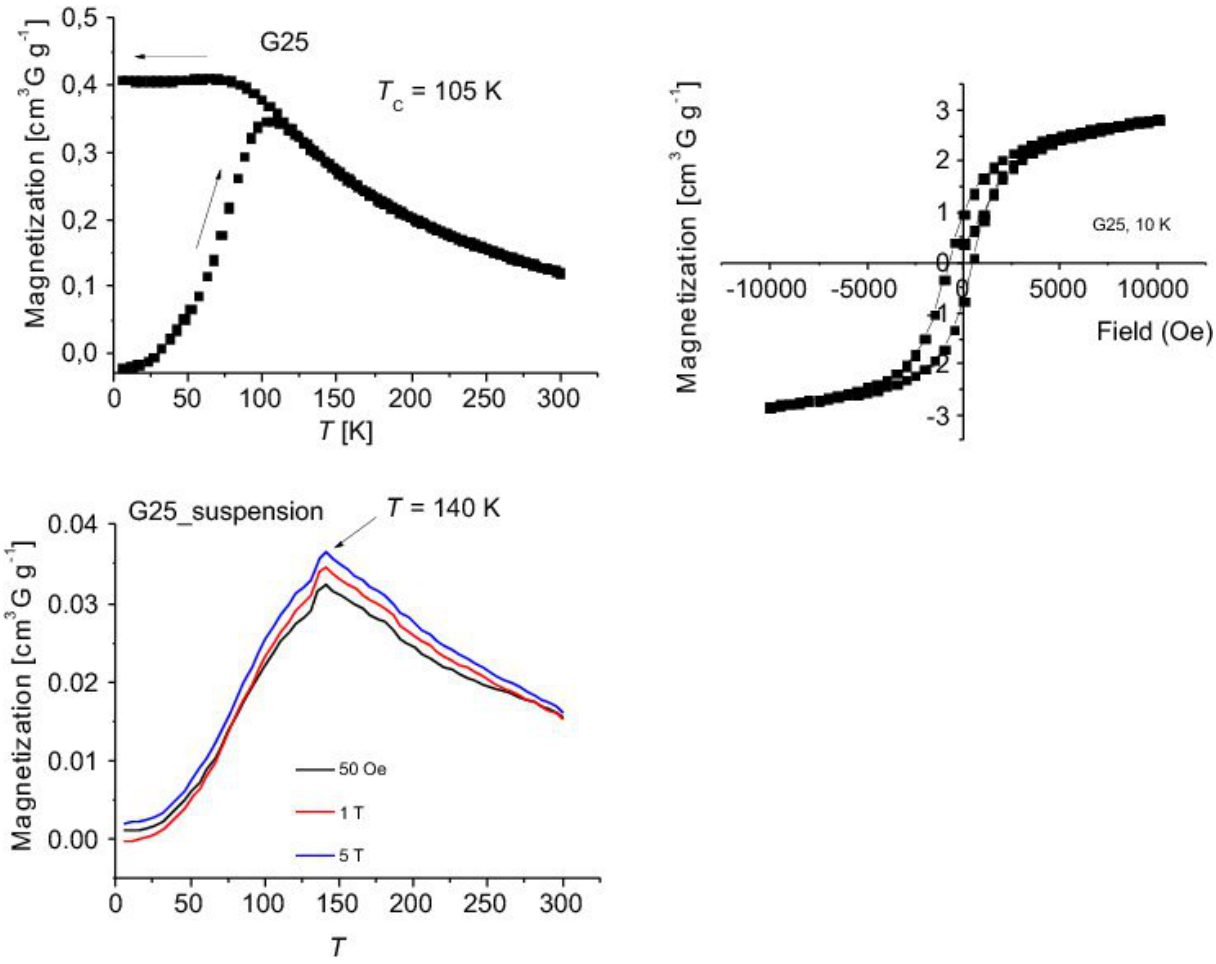

Fig. S9: A) Field-cooled (FCM, 50 Oe) and zero-field-cooled (ZFCM) magnetization measurements of cube-shaped nanoparticles (G25, 8.2 nm) in the dry solid state. The maximum of the ZFCM-curve corresponds to a Curie (blocking) temperature of 105 K. B) In agreement with A), at 10 K a hysteresis loop is observed, but not at 300 K. C) Zero-field-cooled (ZFCM, 50 Oe) magnetization measurements of a solution of the magnetic nanoparticles after magnetization of the sample at 300 K for 30 min with the magnetic field given in the inset. The blocking temperature is shifted to 140 K and a slight increase of the maximum of the magnetization is obseved for increasing external field strengths indicating an influence of the magnetic field on the self-assembly of the particles. The decrease of the magnetization in the FCM-curve below 140 K likely corresponds to spontaneous antiparallel alignment of the magnetic dipoles below the freezing point of the solution.

Magnetic field-induced assembly at higher concentrations

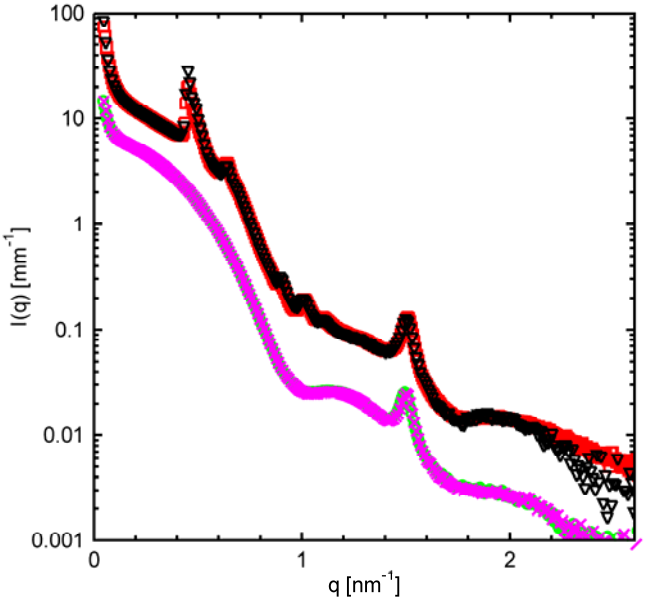

Fig. S10: SAXS-curves showing the influence of concentration on the magnetic field-induced self-assembly of cubic nanoparticles (G102, 7.5 nm). At room temperature, the diluted solution (2 wt%, purple crosses 0 T, green circles 1 T) exhibits a pure form factor scattering, even in the presence of a strong magnetic field, whereas at higher concentrations (11 wt%, red squares 0 T, black triangles 1 T) magnetic field-induced Bragg reflections are observed due field-induced self-assembly.

Mössbauer spectra of magnetic nanoparticles

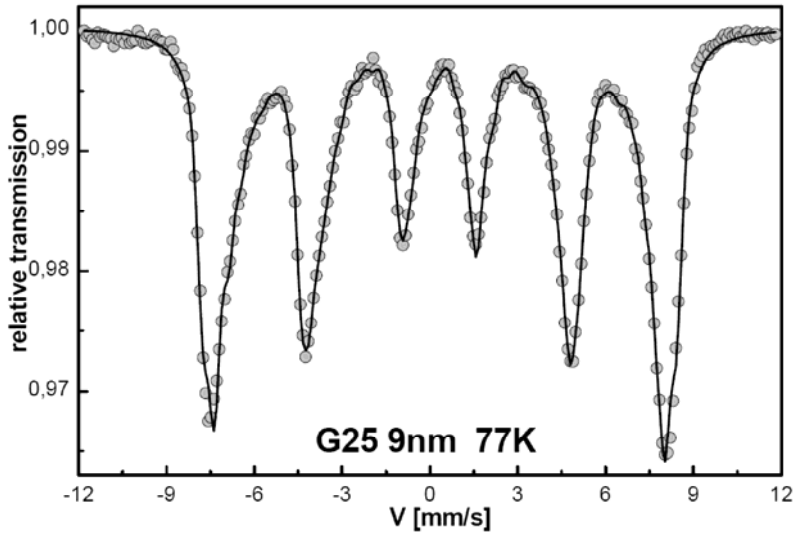

Fig. S11: Mössbauer spectrum of cubic nanoparticles (G25, 8.2 nm) measured at 77 K. We observe the characteristic broadened sextet from Fe^{3+} in tetrahedral and octahedral sites of the iron oxide spinell structure. From quantitative analysis the nanoparticles consist of ~ 60% maghemite (Fe_2O_3) and ~40% magnetite (Fe_3O_4).