On the architecture of multicore iron oxide nanoparticles

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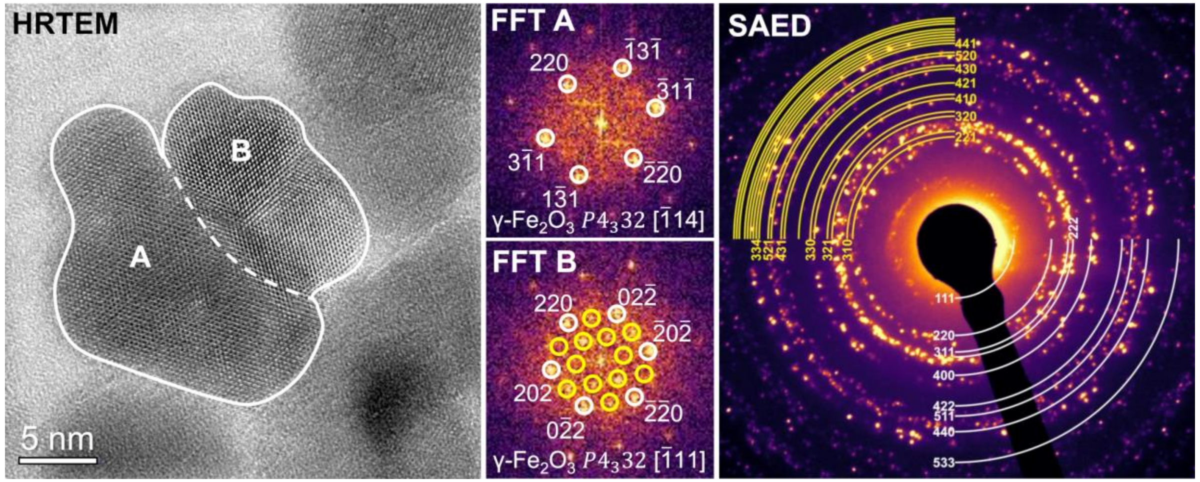
Motivation

Iron oxide nanoparticles (IONPs) are the first choice for applications in biomedicine because of their excellent biocompatibility, biodegradability, easy synthesis and interesting magnetic properties. It has been demonstrated that multicore IONPs show superior properties, for instance a much higher efficiency for magnetic hyperthermia, in comparison to their monocore counterparts. The aim of this work is to reveal the architecture of multicore IONPs, in particular the intergrowth of individual cores within the particles, which plays a tremendous role for their performance.

Materials & Methods

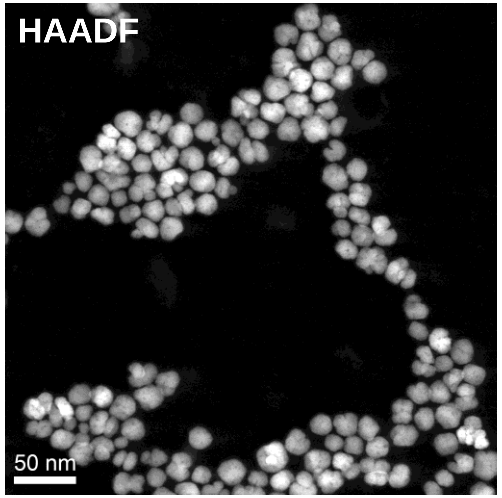
The multicore IONPs investigated in this study are commercially available (synomag-D, micromod Partikeltechnologie GmbH, Rostock, Germany). They were characterized by high-resolution transmission electron microscopy (HRTEM) in combination with local fast Fourier transformations (FFTs), by scanning transmission electron microscopy (STEM) using an upper high-angle annular dark-field (HAADF) detector, by selected area electron diffraction (SAED) and by dynamic light scattering (DLS). The HRTEM images were evaluated by geometric phase analysis (GPA) [1]. Low-magnification HAADF-STEM images were subjected to a semi-automatic segmentation routine [2] for statistical characterization.

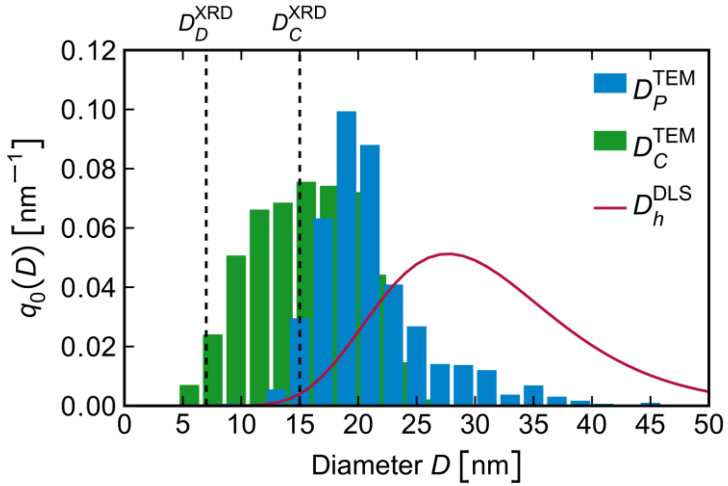
Results & Discussion



- The lattice parameter of the IONPs determined by Rietveld refinement of the XRD data of about 0.8353 nm lies much closer to the bulk lattice parameter of maghemite (0.834 nm, SG $P4_332$) than to that of magnetite (0.839 nm, SG $Fd\bar{3}m$) which indicates that the IONPs are to a great extent oxidized to the maghemite structure.
- The maghemite structure of the IONPs was moreover confirmed by FFT/HRTEM and SAED.
- FFT/HRTEM revealed that the IONPs consist of cores that have orientation relationships which are characterized by the cores sharing major lattice planes, e.g (220) or (311).
- Depending on the lattice mismatch for a specific orientation relationship, the interface between individual cores was found to be either straight or bent.

- Particle as well as core size distribution was determined on the basis of a multistage semi-automatic segmentation routine applied to several low-magnification HAADF-STEM images [2].
- The mean particle size was about 21 nm, the mean core size was about 15 nm.
- The mean size of the particle cores agrees very well with the crystallite size determined by analysis of the XRD line broadening of about 16 nm, which indicates that the cores are crystallographically coherent, while the whole particles are not.
- The mean hydrodynamic diameter of the IONPs was about 31 nm, therefore the mean thickness of the dextran shell can be assumed to be about 5 nm.





References
[1] M. Hÿtch et al., Ultramicroscopy 74 (1998) 131-146.
[2] S. Neumann et al., CrytEngComm, 22 (2020) 3644-3655.
[3] Rafaja et al., J. Appl. Crystallogr. 37 (2004) 612-620.

Acknowledgements
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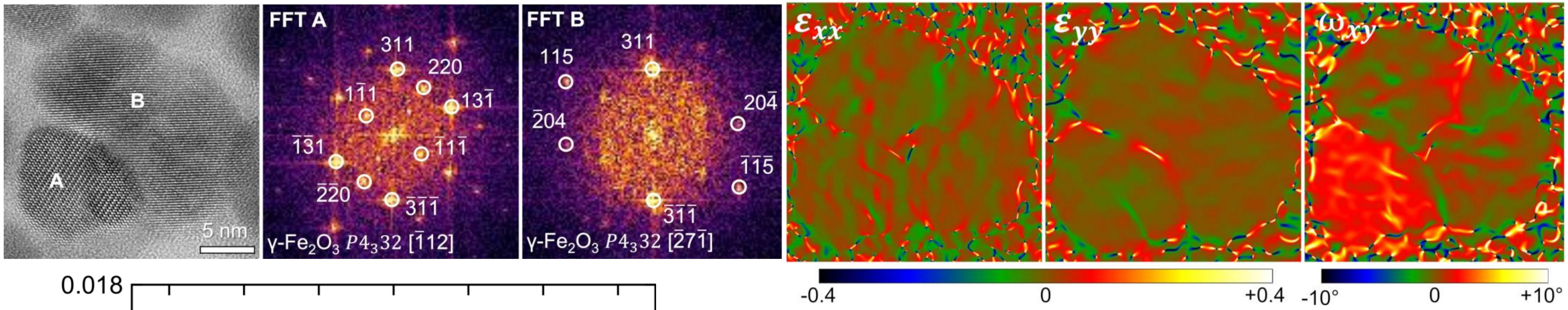
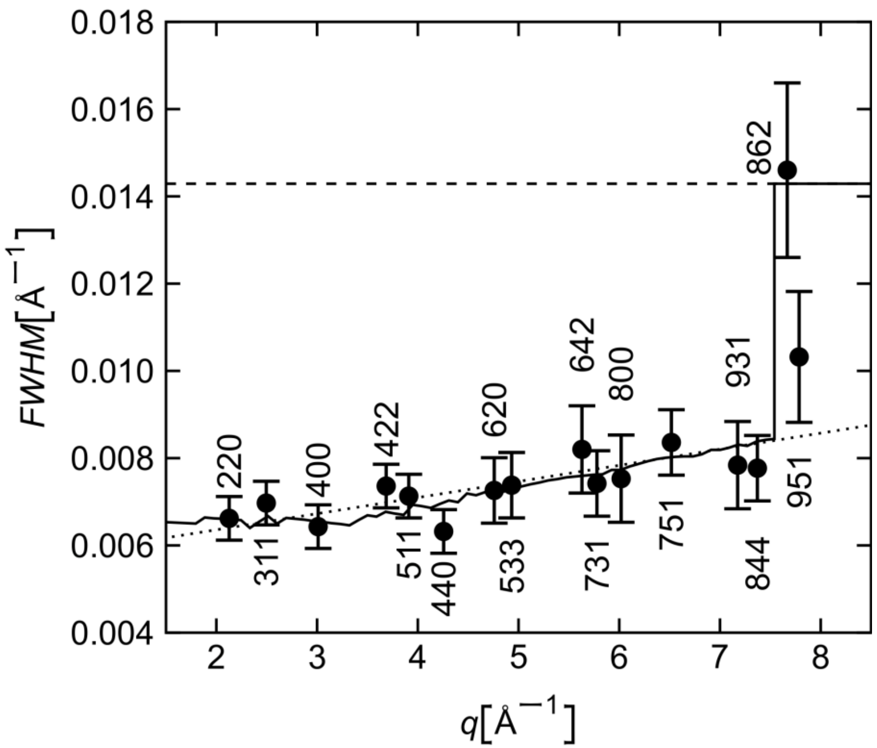
Results & Discussion





» GPA revealed certain strain fields at the interfaces between the cores as a result of the lattice mismatch or a slight twist of the cores with respect to each other (about 2° in the example above)

» GPA moreover revealed that individual cores are further fragmented into domains that are twisted with respect to each other by less then 1° (about 0.3° in the example above)

» Dependence of the XRD line broadening on the length of the diffraction vector can be explained by a partial coherence of the domains of the fragmented cores [3].

» Degree of the coherence of the domains depends on their size and misorientation and is higher at low diffraction angles than at high diffraction angles due to the overlap of reciprocal lattice points which are broadened due to the small crystallite size.

» XRD line broadening was fitted using a theoretical model presented in [3] which provided a cluster size of 16 nm, domain size of 7 nm and a misorientation of 0.25°. The cluster size and the misorientation agree very well with the parameters determined from HRTEM and GPA.

References

[1] M. Hÿtch et al., Ultramicroscopy 74 (1998) 131-146.
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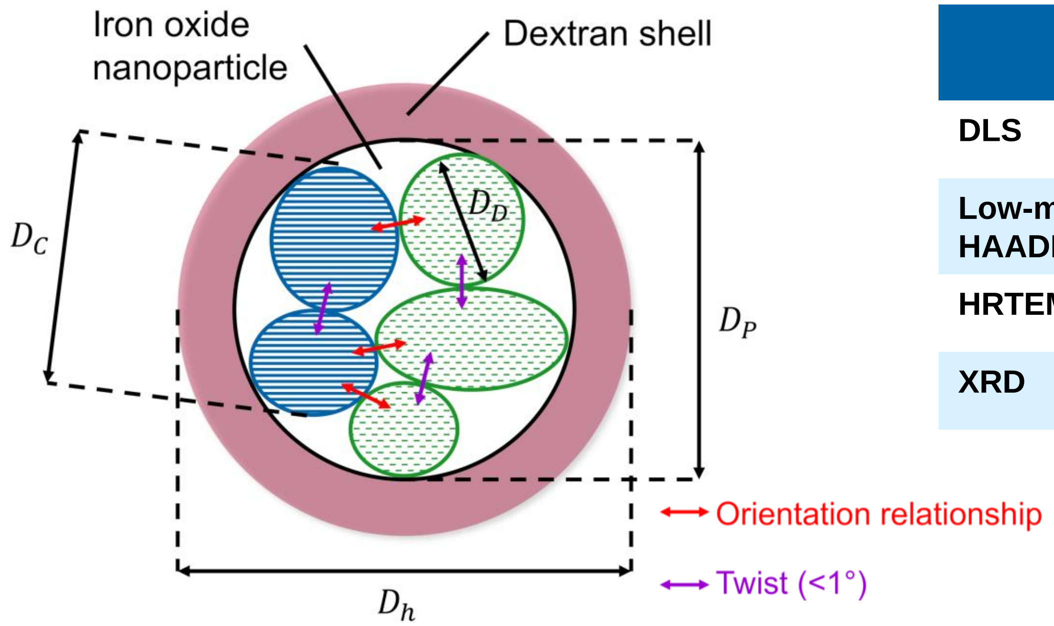
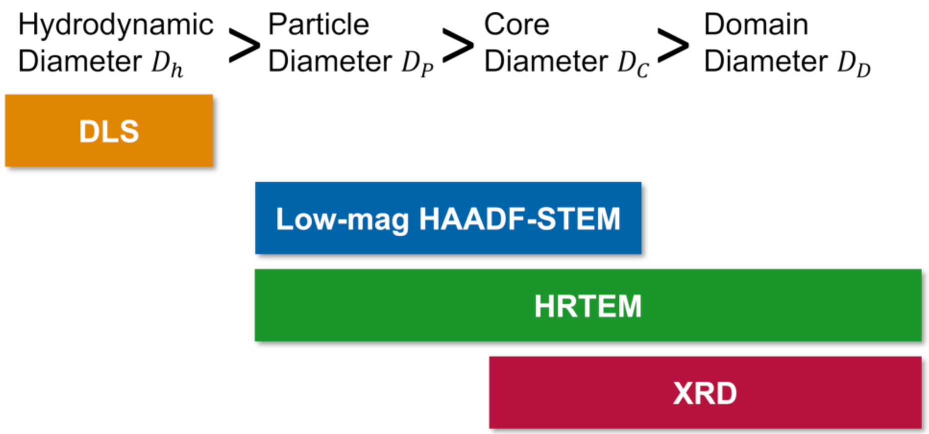
Conclusions





	Hydrodynamic Diameter D_h	Particle Diameter D_P	Core Diameter D_C	Domain Diameter D_D
DLS	31±9 nm	-	-	-
Low-mag HAADF-STEM	-	21±5 nm	15±4 nm	-
HRTEM	-	19±4 nm	13±3 nm	9±3 nm
XRD	-	-	16±3 nm	7±1 nm

» We demonstrated how the combination of HAADF-STEM, HRTEM, XRD and DLS can be used for the correlative size determination of complex nanoparticles such as IONPs and how different characterization techniques are required to determine all different size parameters.

» The combined analysis of the IONPs by the methods mentioned above revealed their hierarchical structure that can be described as follows:

- IONPs consist of maghemite particles with a mean size of about 21 nm and a dextran shell with a mean thickness of about 5 nm.
- One particle consists of several cores with a mean size of about 15 nm.
- Cores within the particles have orientation relationships which are characterized by the cores sharing major lattice planes, e.g (220) or (311).
- Cores are further fragmented into domains with a mean size of about 7 nm.
- Domains within one core are twisted with respect to each other by less than 1°.

» The fragmentation of the cores into domains becomes visible

- directly in HRTEM images and by GPA of the HRTEM images.
- indirectly by the dependence of the XRD line broadening on the length of the diffraction vector as a result of the partial coherence of the domains of the fragmented cores.

References
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