Synthesis of hematite particles monitored using *in situ* SAXS and WAXS

A. Schavkan, F. Westermeier, B. Fischer, I. Steinke, J. Perlich, M. Sprung, and G. Grübel

DESY Photon Science, Deutsches Elektronen-Synchrotron, Notkestr. 85, 22607 Hamburg, Germany

Recent research on colloids and magnetic particles resulted in the development of so-called ”smart nanoparticles”, which show a specific response according to environmental changes (e.g. temperature, magnetic or electric fields). One kind of these smart systems, which is often used as a model system, are magnetic nano-particles consisting out of hematite [1].
The main advantage of hematite particles besides the sensibility to the applied magnetic field is the tunability of the aspect ratio [2]. Although lot of research was performed in order to explore ways to synthesize particles with exact predictable properties and studying the achieved properties themselves, to our knowledge no experiment investigated the hematite particle synthesis *in situ*. Therefore the experiment conducted at the BW4 beamline of the DORIS synchrotron aimed to study the growth of hematite particles *in situ* by small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) simultaneously.
The particles were synthesized according to the method described by Ozaki *et al* [3]. Two syntheses were run simultaneously - one synthesis with the addition of sodium dihydrogen-phosphate, and one without it. While the first synthesis should result in spindle-shaped hematite particles, isotropic particles were expected from the second synthesis.
The reaction suspensions was pumped through a capillary placed in the X-ray beam and then pumped back into the synthesis vessel. A constant magnetic field of 100 mT was applied to the capillaries.

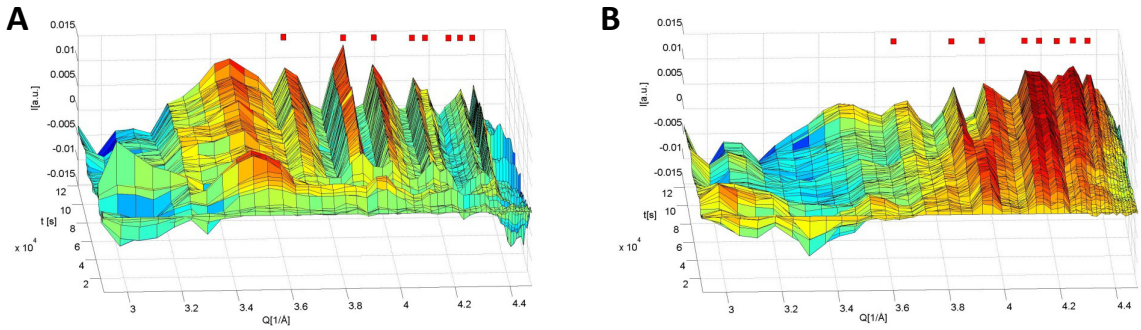

Figure 1: Development of the WAXS signal of the first (A) and second synthesis (B) as a function of reaction time. The stars mark hematite reference peaks.

The WAXS patterns show the development of the different phases in the solution. First only $FeCl_3$ was present in the suspension. During the reaction hematite was synthesized and the WAXS patterns change accordingly, as shown in fig. 1. Depending on the process the development of α-Fe_2O_3 and β-FeOOH was possible [2]. During the performed syntheses, β-FeOOH was not detected.
To align the forming magnetic nanoparticles during the measurements, the experiments were performed in a constant magnetic field. Fig. 2 displays the final SAXS patterns at the end of the two syntheses. In the first synthesis, with addition of sodium dihydrogen-phosphate, indeed spindle-shaped hematite particles developed as expected. The last SAXS patterns of the second synthesis show a four-fold symmetry, which points to a cubic or rectangular shape of the particles. Indeed, a rectangular shape was observed by Sugimoto and coworkers [2] in a similar reaction.

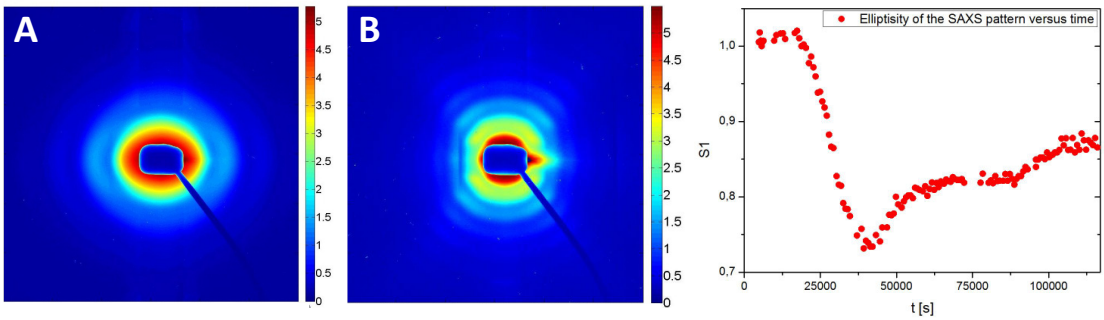

Figure 2: Left: Final SAXS pattern of the first synthesis. Center: Final SAXS pattern of the second synthesis. Right: Ellipticity of the SAXS patterns of the first synthesis as a function of elapsed reaction time.

The synthesis of the spindle-shaped particles finished after 10 hours, while the synthesis of the cubic shaped particles lasted for nearly 32 hours. The *in situ* SAXS study revealed the growth of the hematite particles and the increasing influence of the magnetic field on the forming particles. For the first synthesis, as a measure of the alignment of the sample the ellipticity of the SAXS pattern was calculated, as shown in fig. 2, right hand side. An ellipticity of 1 is equal to a completely disordered orientation of the particles (circular SAXS pattern). If the ellipticity is smaller than 1, the particles are aligned. It was observed that the alignment was increasing first, but decreasing again after approximately 700 minutes. This finding will be investigated in following experiments.

References

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