	Experiment title: High time-resolved SAXS/WAXS of cluster and nanocrystal growth during size-focused inorganic nanoparticle synthesis	**Experiment number**: **MA-3802**
Beamline: BM26B	**Date of experiment**: from: 10.11.2017 to: 14.11.2017	**Date of report**: 25.02.2020
Shifts: 12	**Local contact(s)**: Daniel Hermida Merino	*Received at ESRF:*

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Report:

Summary:

Our experiments aimed to perform highly time-resolved in situ measurements of cluster formation, nanoparticle (NP) core, and crystal growth for the diffusion-limited (size-focused) synthesis of monodisperse superparamagnetic metal oxide nanoparticles. Mechanistically understanding the control over particle growth and final size, and in particular, the growth of the crystalline part of the ligand-coated core is crucial to optimize synthesis conditions for nanocrystals of many different compositions. The high time resolution available from the detectors allowed us to detect the nucleation steps with second time-resolution. Several chemically related syntheses were performed to elucidate the synthesis pathway and thereby complete our understanding of the formation of magnetic metal oxide nanoparticles by the ligand-assisted heat-up method.

Samples and setup

Setup: This experiment used the BM26B beamline. A monochromatic x-ray beam of 12 keV was used and collimated using a series of slits to define a 1x1mm² beam at the sample position. We used a custom-built setup to perform in-situ nanoparticle synthesis next to the setup and progressively monitor the state of the reaction with a flow-through SAXS/WAXS cell. The reaction product was pumped from the reaction vessel with a peristaltic pump. The flow was monitored using a Coriolis flow meter. Measuring the flow rate was instrumental in maintaining the rate of withdrawal of the sample, in being able to deal with blockage and in allowing us to reconstruct the time-axis of the collected sample aliquots. The withdrawn samples were collected in Eppendorf vials using an autosampler for ex-situ analysis, and a UV-VIS spectrometer was integrated into the setup as well to perform chemical analysis of the reaction products. Figure 1a shows a picture of the setup.

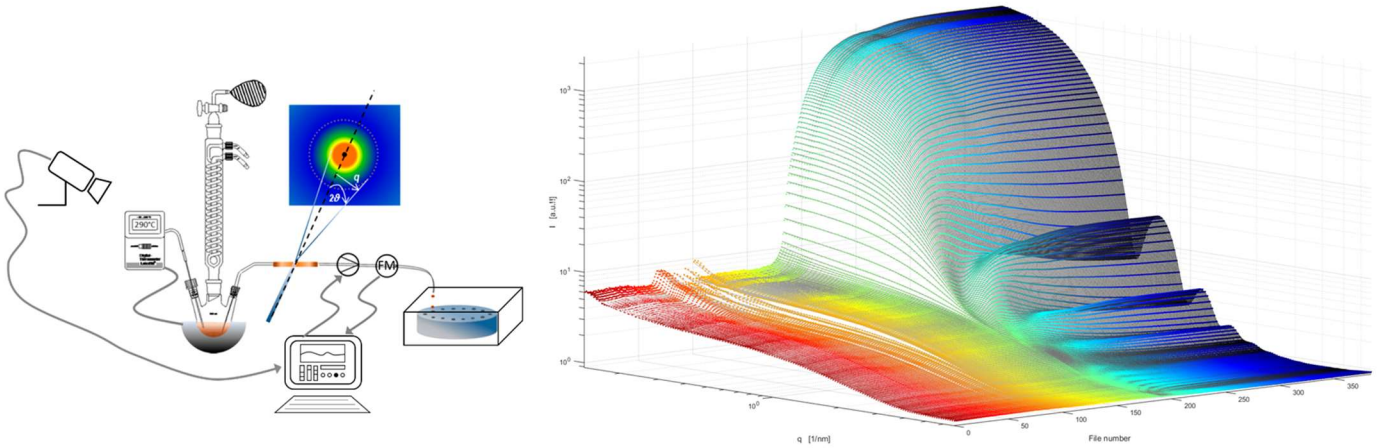

Figure 1a. Schematic of the setup and (b) waterfall plot of a FeOleate synthesis run

The experiment was designed to collect SAXS and WAXS simultaneously with a Pilatus 1M detector for SAXS and a Pilatus 300K-wide for WAXS. An exposure time of 0.2 s was chosen throughout the experiment.
Samples:
The synthesis started from Fe and MnOleate respectively, varying molar ratios were dissolved in Dioctylether and subjected to heating rates of 1, 3 and 9 K/min to final temperatures of 290deg C where the synthesis was held for 60 min to follow the evolution of the nanoparticles. The sample volum was chosen in a way that less than 10% were removed during the experiment.
The Fe-pentacarbonyl experiments followed previously published protocols [1] but we encountered problems to follow the core formation through the complete time series due to blocking of the tube.

Principal outcome

We carried out 18 synthesis runs in total, of which the Fe-oleate (5 runs), Mn-oleate (6 runs) and Fe/Mn-oleate(2 runs) were successful and the Fe-pentacarbonyl (5 runs) were unsuccessful. Despite successful test runs of our setup before the ESRF experiments, we had major problems with clogging of the tubing for the Fe-pentacarbonyl experiments and were not able to resolve this during the beamtime.
The successfully recorded data, however, is of excellent quality. An example dataset is shown in Fig 1b where the evolution of the scattering curves can be seen over the course of the experiment. Figure 3 shows two

typical examples of a first analysis of the scattering data for Fe-oleate and Mn-oleate, respectively. They demonstrate one of the major preliminary findings of the study. Namely, while Fe-oleate leads first to the formation of metal clusters that are precursors for the nucleation step for the nanoparticle formation, MnOx nanoparticle synthesis from Mn-oleate precursors progresses without a distinct step of cluster formation. This is important since all previous detailed investigations of the heat-up method have focused on iron oxide nanoparticle synthesis, and we hereby show that important results for that system might not translate even to closely related synthesis protocols.

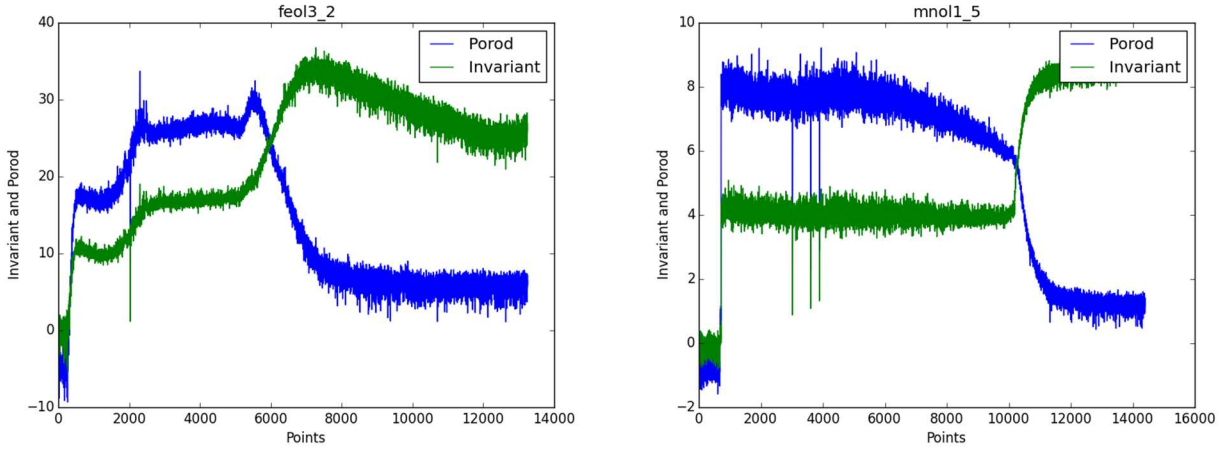

Figure 3. Example Porod constant and Invariant results for a) iron oxide nanoparticle synthesis from Fe-oleate precursors and b) manganese oxide nanoparticle synthesis from Mn-oleate precursors.

Conclusions and further proceedings

We are currently evaluating the data and fitting the reactions to extract integral parameters as well as size, polydispsersity as well as crystallinity and Scherrer width of the reaction products, which will give us deep insights into the early stages of ligand-assisted nanoparticles from metal-organic precursors via the heat-up method.

We anticipate finishing the data evaluation within the next months. We are drafting at least one manuscript based on the obtained results, which most prominently will feature our findings regarding the differences in the importance of cluster formation for the nucleation phase of metal oxide nanoparticle synthesis.

We acknowledge the crititcal support of the PSCM during the preparation of the experiment.

[1] Lassenberger, A; Grunewald, TA; van Oostrum, PDJ; Rennhofer, H; Amenitsch, H; Zirbs, R; Lichtenegger, HC; Reimhult, E. (2017): Monodisperse Iron Oxide Nanoparticles by Thermal Decomposition: Elucidating Particle Formation by Second-Resolved in Situ Small-Angle X-ray Scattering *Chemistry of Materials*. 2017; **29**(10): 4511-452