In situ SAXS investigations of microwave-assisted synthesis of magnetic nanoparticles

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The mechanism of the nucleation and growth of iron oxide nanoparticles (Fe_xO_y-NPs) synthesized by a microwave-assisted solvothermal synthesis approach has been studied simultaneously by small- and wide-angle X-Ray scattering (SAXS/WAXS) and UV-vis spectroscopy. The effect of the reaction temperature, heating rate, role of ligands and solvents on the formation and growth mechanism of Fe_xO_y-NPs and its kinetics have been investigated using a home build high pressure stable *in situ* setup. This setup consists of a polymer tubing system, a syringe pump, a pressure stable UV-vis flow cell (up to 80 bar) and home build polymer flow cells (OD 1.2 mm and ID 1.0 mm, up to 70 bar) for the scattering measurements. One example investigation is the following reaction. The precursor iron (III) acetylacetonate, $Fe(acac)_3$, has been solved in triethylene glycol (TEG) in the molar concentration of 25 mmol/l. The reaction solution was systematically investigated by changing the reaction temperatures from 150, 200, 250 to 300 °C and solution flow rates from 5 ml/min down to 0.3 ml/l. The pressure inside the reaction and measurement setup has reached up to 20 bar. The experiment has been performed in the following way: While starting the microwave heating process simultaneously the withdrawing of reaction solution has been performed in a time-resolved manner out of the autoclave microwave reaction vessels by using a syringe pump. During the withdrawing the colloidal solution has been characterized with a time resolution down to 50 ms by SAXS, WAXS and UV-vis spectroscopy. The increased time resolution has been achieved

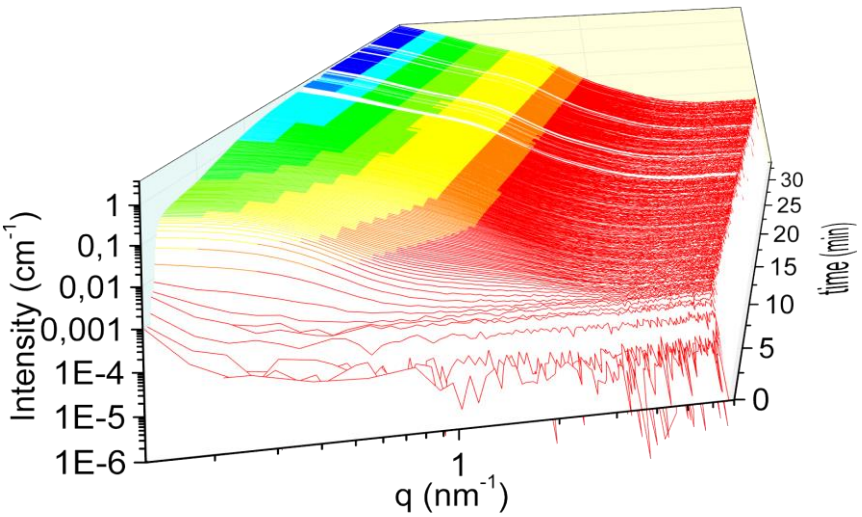

Figure 1 Time-resolved scattering curve waterfall plot of the *in situ* evolution from the iron precursor to the final iron oxide nanoparticles for a 300 C microwave-assisted solvothermal synthesis in triethylene glycol.

by using our home build measurement setup in combination with optimized reaction solution

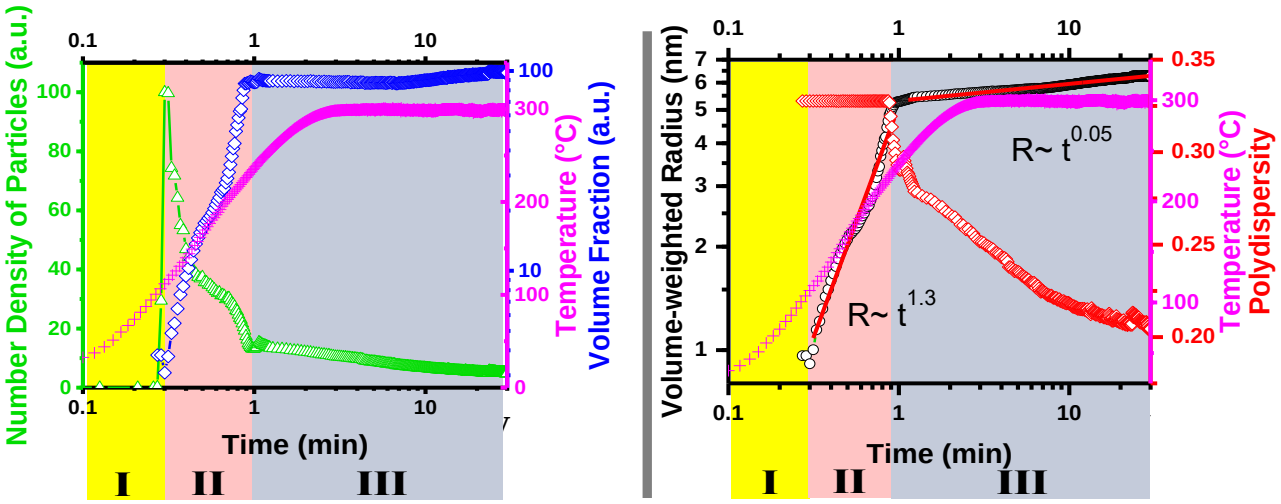

Figure 2 Achieved SAXS analysis for a time-resolved *in situ* formation and growth investigation of microwave-assisted iron oxide nanoparticle synthesis at 300 °C. A three stage formation and growth mechanism was identified. The stages can be distinguished as follows: Stage **I** – reaction of the precursor to clusters; Stage **II** – non-classical rapid growth by coalescence and reaction-controlled growth; Stage **III** – Ostwald ripening. The right diagram contains the radius proportionality to reaction time due to linear fits.

flow rates. The time-resolved scattering curves of one experiment are shown in figure 1. It can be interpreted as the evolution of iron oxide nanoparticles from precursor molecules to nanoparticles with 6.5 nm radius. The achieved data have been fitted using a spherical nanoparticle model with a lognormal size distribution. Figure 2 shows the achieved data from the fits. The logarithmic plotting facilitates the identification of different stages of the formation and growth mechanism for this synthesis approach. Three different stages can be identified. In stage **I** small clusters of the size of typical iron oxide unit cells are formed by a chemical partial reduction. The number density of these clusters increases rapidly to a maximum. In the following stage **II** the number density of these cluster collapse down to 17 % due to a simultaneous non-classical growth of these cluster to nanoparticles by coalescence/aggregation and a reaction-controlled growth of the monomers onto the surface of the clusters/nanoparticles. The result of the linear fit gives a proportionality of R ~ t^1.3. In the last stage **III** of the formation mechanism the nanoparticles are in the Ostwald coarsening stage. The ripening rate is very low, 0.05, due to kinetically hindering by steric organic shells of still coexisting precursor residuals around the particles. This hinders the dissolution, diffusion and growing onto the bigger particles. These SAXS results are supported by *ex situ* TEM and *in situ* UV-vis spectroscopy and WAXS. In this context, UV-vis spectroscopy and SAXS allow characterization of the early stages of NP > 0.5 nm. By using the home build setup in combination with SAXS/WAXS at the beamline DUBBLE BM26b the formation and growth mechanism of the microwave-assisted iron oxide nanoparticle synthesis was successfully clarified in detail. The examined parameter studies of temperature and heating rates gives further explanations into the dependencies of the formation and growth mechanism. The results reveal the fundamentals of nanoparticle formation mechanisms for the investigates system and can be applied to the syntheses of other nanoparticle systems. In conclusion, these findings can improve the synthesis of nanoparticles on demand.