ESRF	**Experiment title:** Concentration-Dependence of ZnO Nucleation Mechanism in the Sol-Gel Process in Methanol via in-situ PDF	**Experiment number**: CH 3868
Beamline: ID-15-B	**Date of experiment**: from: 26th February 2014 to: 1st March 2014	**Date of report**:
Shifts: 9	**Local contact(s)**: Jessica Hudspeth	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M. Zobel *

R. B. Neder *

Institute of Crystallography and Structural Physics

Friedrich-Alexander Universität Erlangen-Nürnberg

Report:

The intial aim of the proposal was to study the precursor structure of zinc oxide (ZnO) nanoparticles in the sol-gel process in methanol, as well as the dependence of this structure on the zinc concentration in solution. In June 2013 we had a beamtime at ID-15-B, during which we ran various experiments in methanol and the results of which are illustrated in the experimental report SC-3602. Therefore, during the beamtime for this proposal CH 3868 we put our focus onto the influence of the amount and speed of the addition of the base tetramethylammonium hydroxide (TMAH) onto the nucleation kinetics of ZnO nanoparticles in ethanol.

The base TMAH was added to a 30 mM solution of zinc acetate dihydrate in ethanol with an externally controlled syringe pump. Two types of experiments have been performed. In the one type we added a finite amount of TMAH in the range 3.0 to 4.5 ml to the solution at once and observed the nucleation thereafter for several hours, see Fig. 1. In the other type we added the overall amount of 4.5 ml TMAH continuously with different speeds of 0.05, 0.15 and 0.25 ml/min and observed the solution during the addition, see Fig. 2. Both types of experiments have been carried out for pure zinc acetate solutions as well as solutions with additional organic ligand molecules such as 1,5-diphenyl-1,3,6-pentanetrione.

Within this report, we want to exemplarily show the results for two examples in Fig. 1 and Fig. 2. The absolute numbers on the G(r) axis are without relevance due to the loss of absolute scale factors between two measurements when processing the data with the PDFgetX3 software. Therefore, only PDFs within one data set can be compared on an absolute scale.

In Fig. 1 the temporal evolution of the ZnO nanoparticle size is shown as it was observed after the addition of 3.2 ml, resp. 4.5 ml TMAH. It is clearly visible that for the smaller amount of TMAH, the nanoparticles seem to nucleate to a finite size and to not grow further. Instead the amount of nanoparticles of that size increases over time which can be derived from the fact that all peaks in the PDF grow equally in height. For the higher amount of 4.5 ml the nanoparticles nucleate to a larger size after about 60 min after base addition. Thereafter, these nanoparticles grow further in size and new nanoparticles only form scarcely, if at all. This is obvious in the unproportional growth of the different peaks in the PDF.

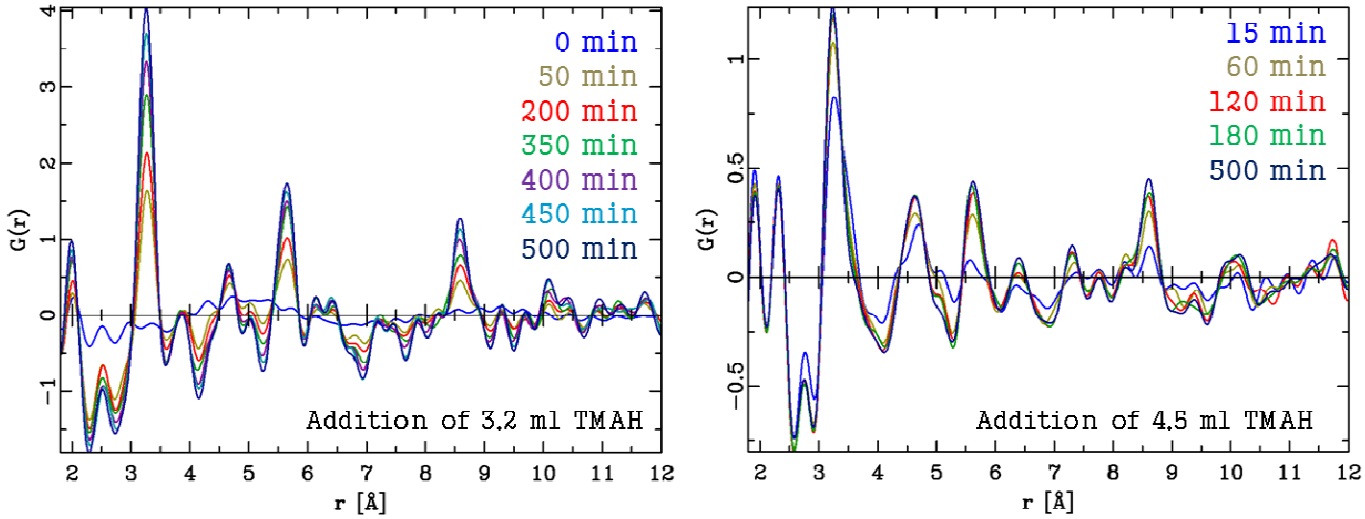

Fig. 1: Comparison of the temporal evolution of ZnO nanoparticle formation after the addition of different amounts of TMAH to the zinc acetate solution

Fig. 2 shows the evolution of ZnO nanoparticles with the additional ligand molecule 1,5-diphenyl-1,3,5-pentanetrione. The ligand stabilizes a smaller nanoparticle size than the one that occurs in pure zinc acetate solutions. In the left plot the TMAH was added at a low speed of 0.05 ml/min in comparison to 0.25 ml/min in the right plot. Comparing the two plots, we conclude that the nanopaticle formation is not solely dependent on the overall amount of the base added, but also on reaction time. For 0.05 ml/min, the nanoparticles need a treshold of almost 1.925 ml[1] TMAH in order to form the first wurtzitic structured clusters. Thereafter, all peaks grow continuously. For the speed of 0.25 ml/min, the base treshold is higher at 2.5 ml[1] and thereafter the nanoparticles do not grow continuously, but spontaneously jump to a very much larger size at 3.125 ml[1] and do not change much afterwards. The difference in the two treshold values for the identical reaction at different speeds of base addition, makes us believe that the nucleation of ZnO nanoparticles not only depends on the concentration of the reactants, but also on the reaction time.

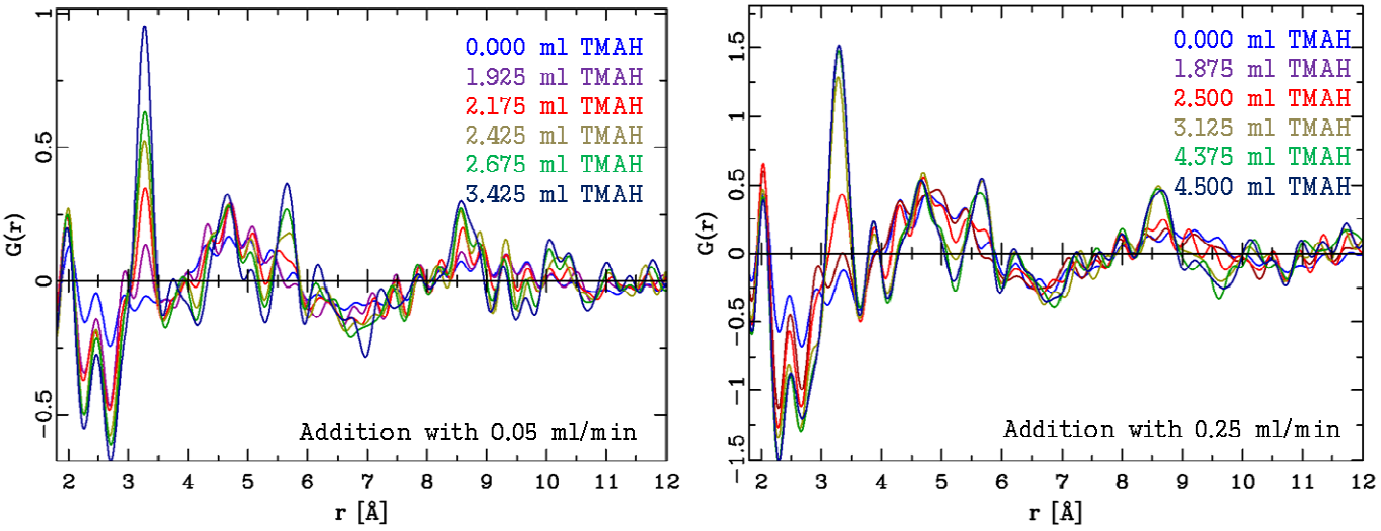

Fig. 2: Comparison of the evolution of ZnO nanoparticles, stabilized with 1,5-diphenyl-1,3,5-pentanetrione, during the addition of TMAH for two different speeds of base addition

More experiments have been carried out for other TMAH amounts and at other speeds of base addition in order to hopefully be able to derive reaction kinetics.

[1] The volume of TMAH added is given so precisely because it was interpolated from the filenumber, i.e. the time which had passed since the first TMAH drop had been added, and given the speed of base addition in combination with a time resolution of 30 seconds per frame, which was required as the lower limit of time resolution in order to aquire high-quality PDF data.