

Early Stages of Particle Formation by In-situ UV-Vis and HRS

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ABSTRACT

We present a new approach for the study of early states of particle formation that can be applied for precipitation processes that occur on timescales from milliseconds to several minutes. A T-shaped micro-mixer is used to precipitate nanoparticles at steady state conditions. The nucleation and growth of the nanoparticles occurs along the path through a transparent quartz capillary. Hyper Rayleigh scattering (HRS) and UV/Vis absorbance spectra are recorded simultaneously. By changing the measurement position along the capillary, different reaction stages of the nanoparticle formation process can be studied in detail. As the precipitation is performed at steady state the integration time for recording signals is not limited by the kinetics of the precipitation process. The HRS intensities and the particle size information can be used to calculate the nucleation and growth rates of the particle formation process.

Keywords: UV-Vis, Hyper Rayleigh Scattering, ZnO, nanoparticle, precipitation

1 INTRODUCTION

The early stages of nanoparticle precipitation are crucial for the morphology and size development as well as for the properties of the final nanoparticles. However, the precipitation process from cluster formation to nanoparticle growth and ripening is not well understood. So far primarily Small Angle X-Ray Scattering (SAXS) and X-ray Absorption Spectroscopy (XAS) have been used to monitor cluster formation and early stages of precipitation [1–3].

In the recent years optical Second Harmonic Generation (SHG) has proven its high potential to probe colloidal nano- and microparticles in-situ with millisecond time resolution. In literature SHG from nanoscaled structures [4] and nanoparticles is also often referred to as Hyper Rayleigh scattering which is typically used for the study of solvated molecules. It has been shown that the HRS signal from nanoparticles is highly sensitive to their size, structure and shape [5]. The Second Harmonic (SH) scattered light is shifted to half of the excitation wavelength. Therefore it can easily be separated from the fundamental excitation light by means of filters and monochromators. With its high time

resolution HRS has the potential for online monitoring of dynamic processes such as growth, ripening and agglomeration of nanoparticles [5,6]. For materials with a high nonlinear response even the formation of molecular clusters can be detected [7].

Recently we have applied HRS to monitor different stages in the synthesis of ZnO nanoparticles. For the ripening process of ZnO nanocrystals the size dependence of HRS was determined quantitatively by a combination of HRS and spectrophotometry. Time-resolved measurements allowed the calculation of nucleation, growth, and ripening rates out of the nonlinear signals [6].

In this contribution we present a new approach for the study of early states of particle formation that can be applied also for precipitation processes that occur on a very short timescale and for nanoparticles that exhibit only a weak nonlinear signal.

2 EXPERIMENTAL SECTION

Ethanol was used for the preparation of all reactant solutions. Before the synthesis, a 0.1 M zinc acetate dihydrate precursor stock solution was prepared and mixed with an equimolar amount of lithium hydroxide at 293 K resulting in an instantaneous particle formation.

The absorbance spectra were measured with a fiber coupled UV-Visible spectrophotometer (Ocean Optics, USB2000+ with DH2000 as light source).

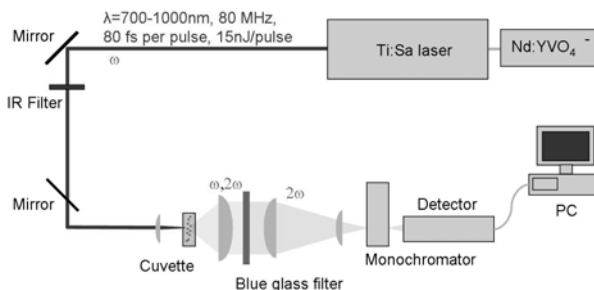


Figure 1: Transmission setup for Hyper Rayleigh scattering experiments.

For monitoring the nanoparticle formation a transmission setup as it is shown in Fig. 1 is used. For

excitation of the Hyper Rayleigh scattering signal a pulsed Ti:Sa femtosecond laser (80 MHz) with a pulse length of about 80 fs and a wavelength of 800 nm is used. For the generation of the HRS signal the beam is focused into a capillary that contains the sample. With a second lens after the probe the scattered light is collected. A blue color filter that transmits only light shorter than 650 nm is used to block the transmitted and linear scattered laser light. The filtered light is then focused into the slit of a monochromator for a further separation of the HRS signal from other background radiation as two photon fluorescence. The HRS light is detected by a photomultiplier tube and recorded by a computer. The precipitation of nanoparticles is either done in the capillary of a flow cell setup as it is shown in Fig. 2.

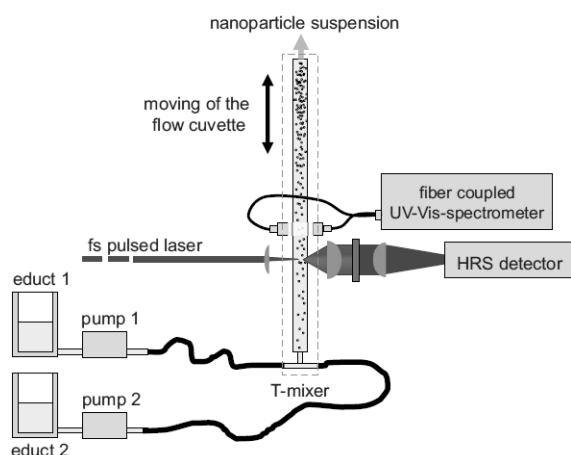


Figure 2: Schematic setup for simultaneous time resolved UV-Vis and Hyper Rayleigh scattering experiments at steady state condition.

A T-shaped micro-mixer is used accomplish a fast mixing of the reactants and to precipitate the nanoparticles at steady state conditions. After the mixing zone the cross sectional area of the capillary is increased and a laminar flow through is formed. The synthesis of nanoparticles occurs along the flow through the capillary. The precipitation setup is mounted on a moveable stage. For monitoring the growth of the nanoparticles HRS and UV/Vis absorbance spectra are recorded simultaneously. By changing the measurement position along the capillary, different reaction stages can be studied in detail.

3 RESULTS AND DISCUSSION

The precipitation of ZnO particles was carried out for different reactant concentrations and at different flow rates. HRS signals and absorbance spectra were measured simultaneously at different positions along the capillary. The measurement position was converted into an average reaction time using the flow rate and the cross section of the capillary. In Fig. 3 the smoothed HRS signal intensities

along the capillary for a flow rate of 5 ml/min and a Zn^{2+} concentration of 0.043 mol/l are shown.

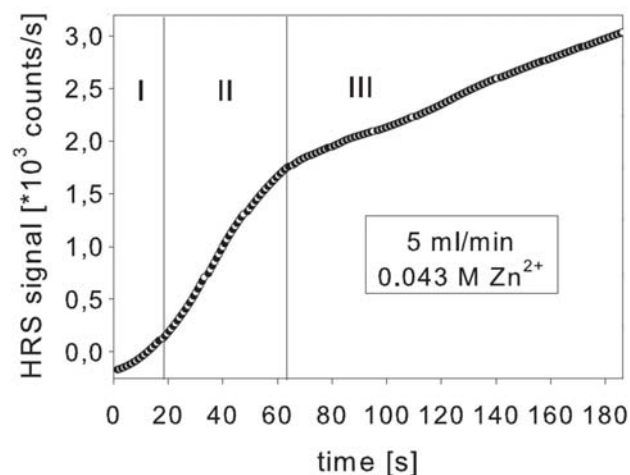


Figure 3: Smoothed HRS signal intensity for the early stages of particle formation.

Three stages can be distinguished. After the initial stage I there is a steady increase of the HRS signal intensity (stage II). In the third stage the slope of the curve changes and a linear increase of HRS signal intensity can be observed. We attribute the first stage to an initial stage of the reaction. Here a supersaturation is build up and primary nuclei are formed. After the build up of the supersaturation, a strong increase of the HRS signal is found in the second stage. The rise in the HRS signal is attributed to an increase of the number of nuclei (nucleation step) and due to the growth of the initial particles. After the formation of primary particles we assume that the number concentration does not change significantly and that the primary particles are growing. This corresponds to the third stage, which is observed after about 60 s (compare Fig. 3).

Absorbance spectra are simultaneously recorded at a distance of 2 cm after the HRS detection zone. From the absorbance spectra, ZnO particle size distributions are calculated by the algorithm that is explained in detail in reference [8]. The respective absorbance spectra are shown in Figure 4.

In the first 10 s of the precipitation, the absorption spectroscopy peak is not clearly formed and only a small and broad peak is observed. A first clear peak forms after 34 s. The absorbance peak increases with reaction time and shifts to longer wavelengths. The absolute value of the absorbance peak also increases and reaches the detection limit of the spectrophotometer after about 40 s.

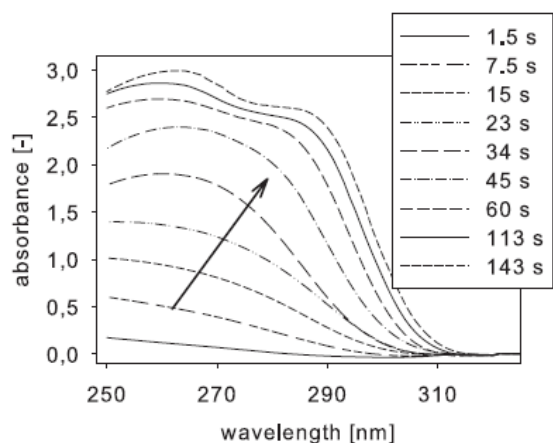


Figure 4: Absorbance spectra from ZnO nanoparticles along the axis of the glass capillary; the reactions times are calculated from the measurement position and the flow rate.

However, for the particle size correlation, the onset of the absorbance peak is most important, thus enabling the processing of the absorbance spectra even at higher levels of the peak absorbance. The calculated particle size distributions for different measurement times are shown in Fig. 5.

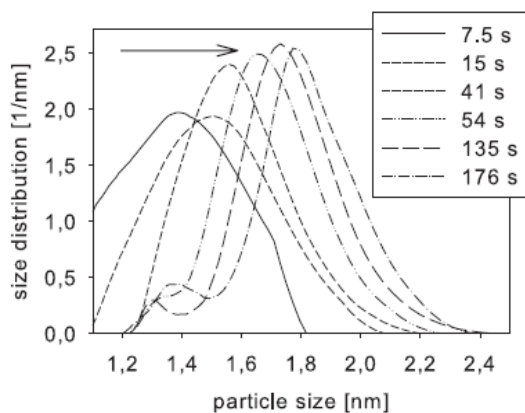


Figure 5: Volume density distribution of the ZnO nanoparticles at different reaction times calculated from the corresponding absorbance spectra.

Furthermore, the dependence of the ZnO hyperpolarizability on the particle size was determined using different measurement positions along the pipe. From the hyperpolarizabilities, the number density of the ZnO particles was calculated for different reaction times. During phase II, a strong increase in the particle number density was found which then proceeds to an almost constant particle number density in stage III. This result indicates that the ZnO precipitation process can indeed be divided into a nucleation and a particle growth stage. The particle

size distributions and the number densities are further on used to determine the nucleation and growth rates of the ZnO precipitation process.

4 CONCLUSION

We have precipitated ZnO nanoparticles using a steady state flow cell setup. With this approach the measurement time is not limited by the reaction kinetics of the precipitation process and the signal-to-noise ratio can be improved significantly. This enables the study of particles that exhibit only a weak nonlinear response. For the precipitation of ZnO particles we were able to characterize particles as small as 1.6 nm. The mean particle sizes and size distributions were calculated from the absorbance spectra. The combination of absorbance and HRS experiments can be used for the quantitative determination of nucleation and growth rates.

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REFERENCES

- [1] F. Meneau, G. Sankar, N. Morgante, R. Winter, C. R. A. Catlow, G. N. Greaves, J. M. Thomas, *Faraday Discuss.* 122, 203, 2002.
- [2] J. Rockenberger, L. Träger, A. Kornowski, T. Vossmeier, A. Eychmüller, J. Feldhaus, H. Weller, *J. Phys. Chem. B* 101, 2691, 1997.
- [3] P.-P.E.A. de Moor, T.P.M. Beelen, R.A. van Santen, *Micropor. Mat.* 9, 117, 1997.
- [4] L. Martinez Tomalino, A. Voronov, A. Kohut, W. Peukert, *J. Phys. Chem. B* 112, 6338, 2008.
- [5] K. Das, A. Uppal, P.K. Gupta, *Chemical Physics Letters* 426, 155, 2006.
- [6] D. Segets, L. Martinez Tomalino, J. Gradl, W. Peukert, *J. Phys. Chem. C* 113, 11995, 2009.
- [7] M.C. D'Arrigo, Cruickshank F. R., Pugh D., Sherwood J. N., Wallis J. D., Mackenzie C., Hayward D., *Phys. Chem. Chem. Phys.* 8, 3761, 2006.
- [8] D. Segets, J. Gradl, R.K. Taylor, V. Vassilev, W. Peukert, *ACS Nano* 3, 1703, 2009.