| ESRF | **Experiment title:** Time-Resolved Parameter Dependent Study of Silver Nanoparticle Growth Processes | **Experiment number:** SC-3383 |
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| **Beamline:** ID02 | **Date of experiment:** from: 23 July 2012      to: 27 July 2012 | **Date of report:** 31st Aug 2012 |
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During the last decades metal nanoparticles have attracted much attention. The enonourmous scientific interest results from their potential for a variety of interesting applications which are based on their unique catalytic, electronical, biological and optical properties.[1] These properties are determined by the particle size and shape. Thus, precise control over size and morphology provides an effective way to tune the properties of nanomaterials for a desired application. As a result, many studies are focused on the development of syntheses that enable size control. The most common strategy is to vary synthesis parameters (e.g. concentrations, temperature, ionic strength) systematically and to determine the final size distribution. Although this trial-and-error approach can provide useful information, the actual way the parameters influence the growth mechanism and thus the final size distribution remains a *black box*.[2] In contrast,this project it was intended to elucidate the processes that govern particle growth to improve the size control for a certain synthesis. In addition, fundamental principles of colloidal growth and stability can be deduced when investigating different syntheses.

Such an approach demands the availability of experimental data about the evolution of particle size and concentration. Small Angle X-Ray Scattering (SAXS) is the appropriate method not only to investigate the final size distribution of a colloidal solution but also to study colloidal growth in-situ and time-resolved. As one of the few beamlines worldwide, ID02 offers an extremly high time resolution of up to 50 ms which enables the investigation of particle growth in detail. Furthermore, the combination of time-resolved SAXS with a Free Liquid Jet setup allows to monitor particle formation without contamination of container walls or X-Ray inducing effects.[3]

Within the scope of project **SC-3383** we investigated the growth of silver nanoparticles synthesized by a simple wet-chemical reduction ($AgClO_4$ reduced by $NaBH_4$). From lab-scale experiments the principle growth mechanism for this system could be deduced. [4] It comprises a fast and complete reduction of the silver precursor followed by the formation of small clusters. Immediately, these clusters undergo a coalescent process which results in particles of approx. 2 nm mean radius. After a metastable state the preliminary

formed particles are subject to a rapid stability loss. The result is a further coalescent step which leads to the final colloidal solution with particles of 5-10 nm mean radius.
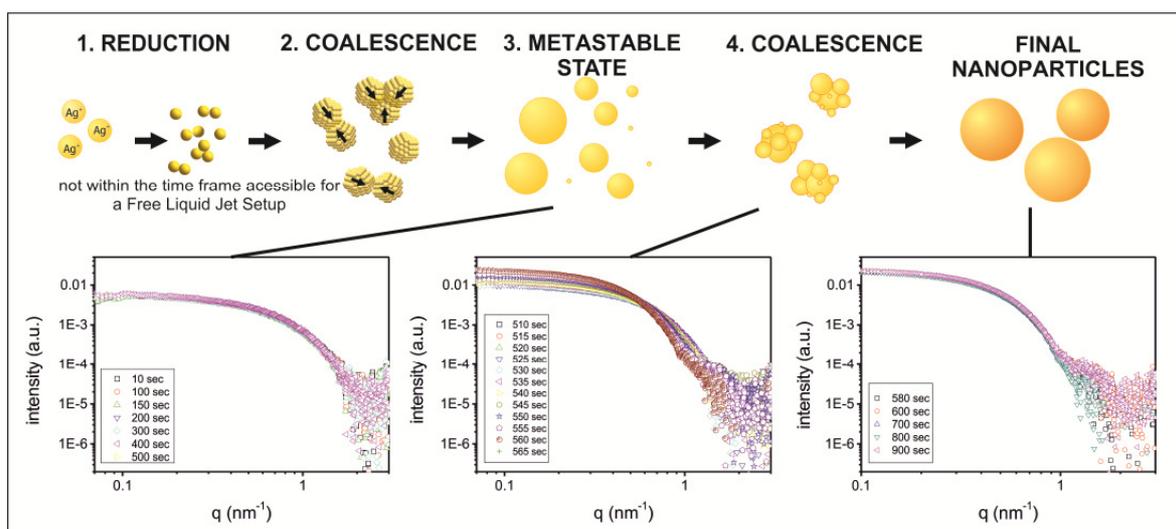


Figure 1: Deduced silver nanoparticle growth mechanism with selected scattering curves corresponding to different steps of nanoparticle formation.

At the ID02 beamline, the growth process was studied with a time resolution of 5 s which cannot be provided by a lab-scale SAXS instrument. Figure 1 displays selected scattering curves for the mechanistic steps that follow the first coalescent process. The first coalescent step itself cannot be investigated using a Free Liquid Jet setup since it occurs on a time scale below the dead time (approx. 10 sec). However, with these measurements it is in particular possible to follow the second coalescent process. This enables the investigation of an important influence on the growth mechanism: the age of the reducing agent solution. That is the time between the dissolving of the solid sodium borohydride in water and the use of the solution to reduce the silver precursor. After dissolving, $BH_4^-$ immediately reacts with water to form hydrogen and $B(OH)_4^-$. Hence, the ratio $[BH_4^-]/[B(OH)_4^-]$ decreases with the age of the reducing agent solution. With lab-scale experiments the influence of this aging process on the final particle size distribution was investigated (see figure 2). A complicated correlation between age and final size distribution was observed including a plateau of approx. 200 min during which the final particle mean radius remains almost constant. The change of the growth mechanism was studied at ID02 for different aging times. Figure 2 displays the size evolutions for selected points. It was found that the duration of the metastable state decreases with increasing aging time (compare A and B) until both coalescent steps merge to one (see C). The plateau is a result of a merging of the two separated coalescent steps and thus a mechanistic change with direct impact on the final particle size distribution and the reproducibility of the synthesis. Furthermore, it was found that the borate species have a strong impact on the growth process and thus the final size distribution. By adjustment of this parameter, the final size can be tuned.

In summary, highly time-resolved monitoring of the particle size evolution during a silver nanoparticle synthesis provided important information on the influence of the aging process of the reducing agent solution and the hydrolysis kinetic on the nanoparticle formation. In general, to investigate the influences of parameters on the growth mechanisms rather than to simply test their impact on the final size distribution is a promising approach for a variety of nanoparticle syntheses. The investigation of nanoparticle formation with synchrotron SAXS during the very first seconds remains challenging since the Free Liquid Jet setup is limited by a deadtime of approx. 10-20 sec and stopped-flow setups can induce particle agglomeration at the capillary walls. Thus, novel setups for SAXS experiments need to be developed which enable container-free

measurements with a short deadtime. Moreover, the comparison of different reaction systems (different metals, precursors, reducing agents, steric stabilizers etc.) might allow to deduce fundamental principles of nanoparticles growth. Hence, the growth mechanisms of a variety of further systems need to be investigated.
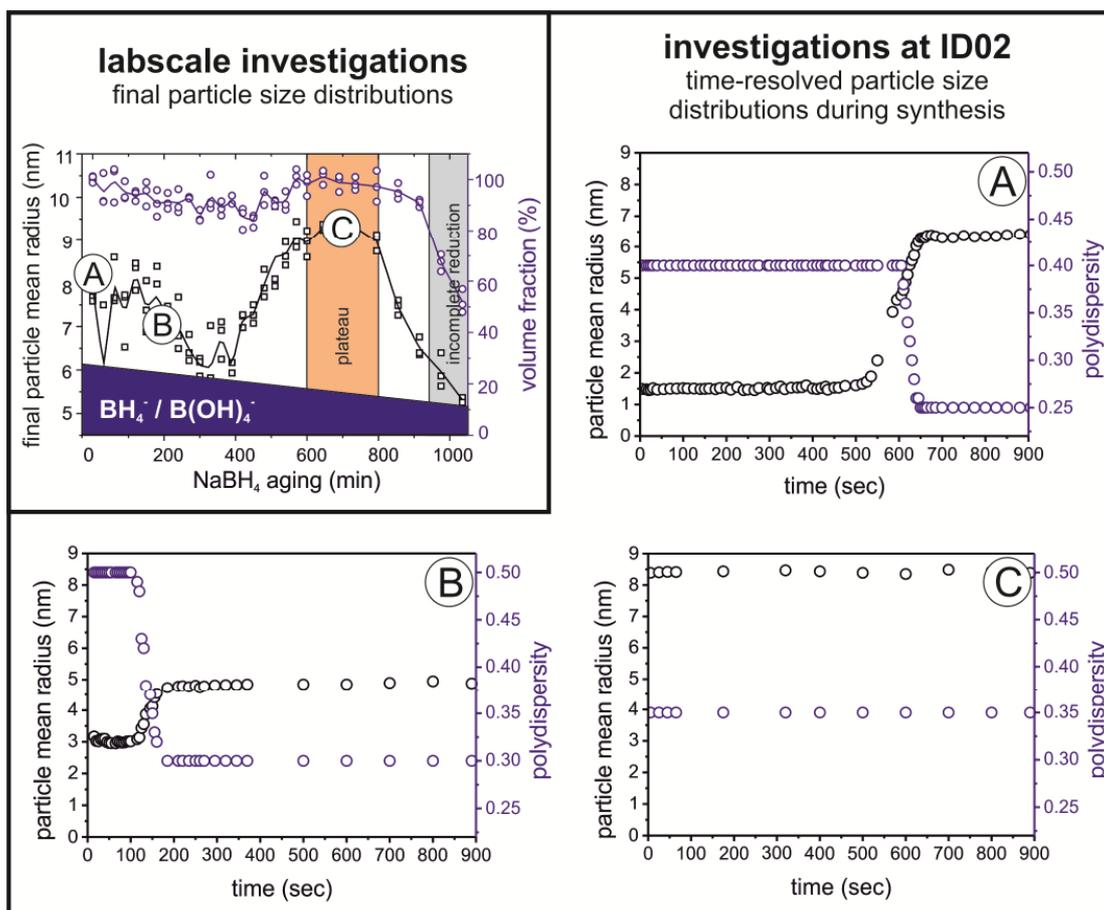


Figure 2: Final size distributions vs. the age of the reducing agent solution from labscale investigations. The evolution of nanoparticle size during formation investigated time-resolved with synchrotron light source at selected points.

# References

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