SAXS-Studies of Silver Nanoparticle Growth Processes

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Metal nanoparticles have attracted much attention in modern science and technology. The control of particle size and morphology enables the adjustment of their properties which is the requirement for a broad range of applications. As a result, many studies focus on size control but are mainly based on simple trial-and-error approaches while the underlying growth mechanisms remain widely unknown. [1] However, a deep understanding of the processes that govern colloidal growth provides the key to syntheses with improved size control. SAXS is an 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.

From preliminary lab-scale experiments, we elucidated the principle growth process of silver nanoparticles synthesized by chemical reduction of aqueous AgClO₄ solution with NaBH₄ [2]. Initially, the ionic precursor is reduced rapidly (<1 s) to silver atoms. The silver atoms form dimers, trimers and so on and coalesce further until they reach a certain level of stability. After a metastable phase (after 5-15 min) in which the particle size distribution does not change (mean radius 1-2 nm), a second coalescent event is observed. This leads to the final colloidal solution with spherical particles of 6-8 nm in radius. The different steps of growth can even be observed visually (see Fig. 1a) since silver nanoparticles larger than 3 nm in radius exhibit a characteristic surface plasmon resonance.

To advance the understanding of the growth mechanism and its kinetics, SAXS measurements were performed at the P03 beamline by applying a Free Liquid Jet setup [3]. As one of the few beamlines worldwide P03 offers an extremely high time-resolution in the millisecond regime which is necessary to monitor the growth process in detail. Fig. 1b shows selected scattering curves along with corresponding fits for spherical particles and the derived results (Fig. 1c). It reveals that the particle size distribution remains constant during the entire metastable phase. The second coalescent step proceeds within approx. 60 sec. A process of coalescence demands a process of aggregation which is the consequence of an insufficient colloidal stability. Thus, it can be assumed that growth of the silver nanoparticles formed during this synthesis is governed by colloidal stability.

To understand the synthesis in more detail, the influences of synthesis parameters on the final size distribution were investigated at the B1 beamline. We could show that the principle growth mechanism persists for all investigated parameter combinations. The ratio of precursor and reducing agent was found to have a significant influence on (i) the duration of the metastable state which was observed visually and (ii) the final size distribution. The first finding can be attributed to a temporary stabilization of the primary formed particles by residual BH₄⁻. Tetraborohydride is converted to B(OH)₄⁻ during the metastable phase. Therefore, the stabilization decreases during the metastable state leading to the second coalescent event (point of insufficient stability). The second finding shows that the BH₄⁻ and B(OH)₄⁻ ions have a strong influence on the electrostatic stabilization of the nanoparticles since coalescence is the consequence of insufficient colloidal stability.

In summary, the formation process comprises two well distinct steps of coalescence which are determined by the electrostatic stabilization available in the colloidal solution. This electrostatic stabilization is governed by the borate species. This understanding was available from a combination of time-resolved SAXS experiments and parameter variation studies and is of fundamental interest in colloidal science. It paths the way to the development of strategies for size-controlled syntheses as size determining parameters are identified. This approach is also promising for other nanoparticle syntheses.
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Figure 1: a) Photographs of the colloidal solution during synthesis. b) Selected scattering curves and fits for different reaction times. c) Mean radius and polydispersity vs. time.

References