Size Controlled Synthesis of Silver Nanoparticles Based on Mechanistic Knowledge

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Abstract

Metal nanoparticles have become a focus of extensive research due to their unique catalytic, optical and magnetic properties. Besides composition, crystal structure and morphology, these properties strongly depend on the particle size.[1] Thus, size control provides one effective key to an accurate adjustment of colloidal properties. Unfortunately, synthetic procedures for metal nanoparticles with size control are rare, especially for silver nanoparticles.[2] Most syntheses are based on the chemical reduction of a precursor salt by a reducing agent such as sodium citrate or sodium borohydride and mostly demand the addition of a stabilizing agent. The common approach to size control is a simple trial and error testing of different reaction conditions. The particle growth mechanisms and in particular the parameter influences on the growth remain a black box although such knowledge can provide the key to a well-directed development of synthetic procedures for nanoparticles on demand.[3]

In this contribution we present a general approach to size control which is based on mechanistic knowledge. The approach comprises three steps: (1) the investigation of the principle growth mechanism including all relevant physicochemical processes for one combination of parameters, (2) the investigation of parameter influences on the growth mechanism leading to the identification of size determining parameters and (3) the deliberate adjustment of the decisive reaction parameters to obtain a desired final particle size distribution. The approach is exemplified for a silver nanoparticle synthesis (wet-chemical reduction of $AgClO_4$ with $NaBH_4$).

Recently, we deduced the principle growth mechanism from time-resolved in-situ SAXS investigations (illustrated in Figure 1).[4] It comprises (1) the rapid reduction of the ionic silver, (2) the coalescence of these preliminary formed clusters, (3) an intermediate phase of stability and (4) a second coalescence which is the result of the complete conversion of residual BH_4^- to $B(OH)_4^-$. The final particle mean radius of the spherical colloids ranges from 4 to 9 nm and is poorly reproducible.
In the next step of the approach, the influences of reaction parameters on the growth mechanism were elucidated.[5] The age of the reducing agent solution was found to have a major impact on the growth mechanism. Upon dissolving solid $NaBH_4$ to prepare the reducing agent solution, BH_4^- immediately reacts with water to give $B(OH)_4^-$. A decreasing ratio $BH_4^-/B(OH)_4^-$ (which corresponds to an increasing aging time of the reducing agent solution) causes a merging of the two separated coalescent steps. The change of the growth mechanism leads to a highly improved reproducibility of the nanoparticle synthesis. In addition, the final particle size is strongly affected by the ratio $BH_4^-/B(OH)_4^-$.
Thus, from these investigations a synthetic procedure could be deduced that enables the reproducible synthesis of silver nanoparticles in water in a range from 5 to 12 nm in radius. To the best of our knowledge, this is the first time that silver nanoparticles which do not require additional stabilization agents can be produced with controllable size in this range.

References

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Figures

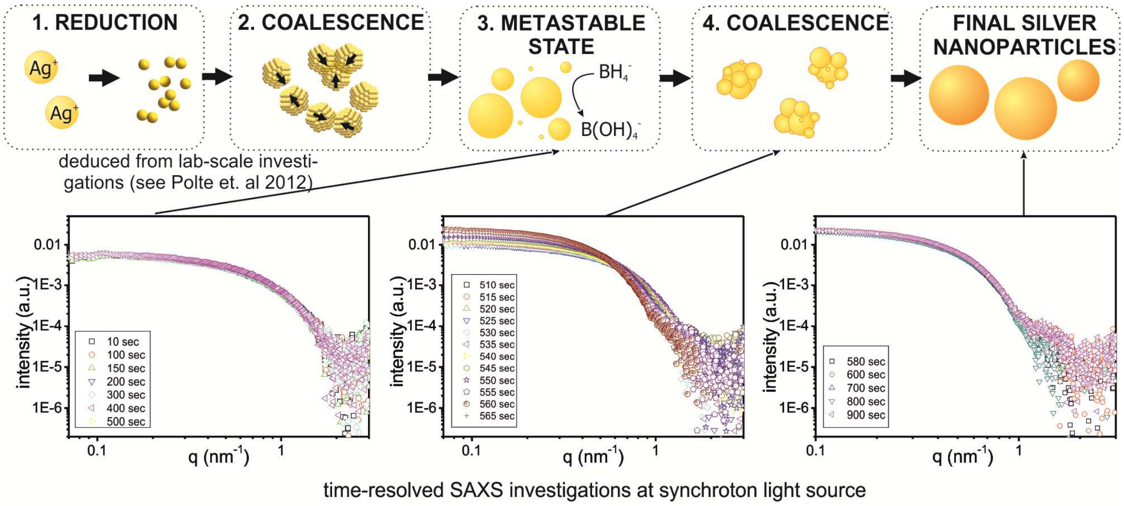

Figure 1: Particle growth mechanism for the reduction of $AgClO_4$ with an excess of $NaBH_4$ deduced from time-resolved Small Angle X-Ray Scattering (SAXS) experiments with selected scattering curves.