ESRF	**Experiment title:** **Structural kinetics of nanoparticle synthesis II (slow part)**	**Experiment number**: SC 2060
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Report:

The aim of the present experiment was to resolve the nanoscopic mechanisms of metal nanoparticle formation during a typical procedure that is frequently utilized in various chemical routes to nanoparticle synthesis.
The general problem consists in the fact, that the procedure is described by a number of subsequent steps, of chemical reduction, nucleation, growth or ripening phenomena. The interplay of these steps largely determines the final sizes, shapes or other morphological properties of the particles [1]. Although there are decades of work devoted to this problem, no detailed understanding of the process is available, in particular concerning the atomic scale and nanoscale structure evolution.
We studied an apparently simple system, the Turkevich reduction method, which yields rather monodisperse gold particles, whose sizes can be tailored by the concentration of the reductant, which is typically sodium tris-citrate. Despite a seemingly simple reaction of reducing gold ions to neutrals and let them cluster together both on the chemical side and on the clustring side several kinetic steps are present, that lead to an enrolement of the synthesis on a time scale that spans 15 decades in time: (photo)reduction of trivalent gold ions to divalent ions on a picosecond time scale, disproportionation reactions to form neutrals on the microsecond time scale, clustering of atoms to primary particles on the second scale, formation of secondary particles on the minute scale and finally particle smoothing and ripening on the hour scale.
The setup was designed to premix a solution of gold hydrochlorate with citrate at a defined concentration with the possibility of adding PVP polymers as strong stabilizer for small particles, then start the x-ray exposure of a fixed aliquot simultaneously with UV irradiation, that provides the initiation of the reaction by converting Au(III) to Au(II). Thereafter the following reaction is found to enrole on the minute to hour time scale as established in optical experiments [1].
Therefore the CCD camera was exposed and read out at fixed rate, which could be as fast as 0.5 Hz while utilizing exposure times of 0.05 – 0.2 seconds depending on the scattering power of the sample.

We recorded small angle scattering at two detector distances in order to allow for a different resolution ranges. The larger distance at 5m from the sample at 12 keV was necessary due to the large final sizes of the particles (in the range of 20-40 nm) in order to allow to record the Guinier region.

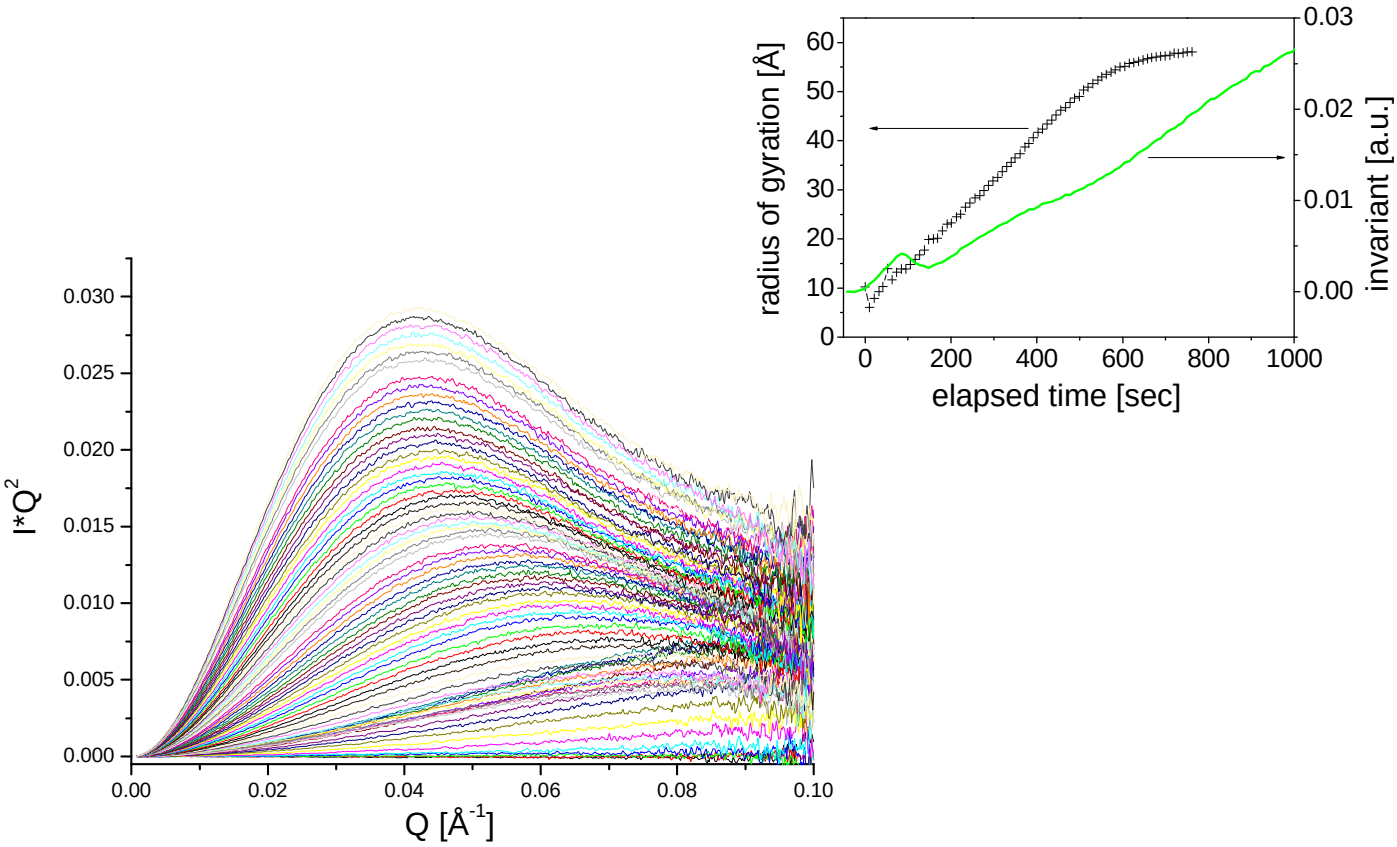

Fig. 1: Series of SAXS profiles of the solution of growing nanoparticles for different elapsed times after the start of the photoreduction in a Kratky representation. The upper left plot shows the radius of gyration together with the invariant (q scaled integral over the scattering curve)

As expected we could observe the particle growth, which is smooth in terms of size (the radius of gyration increases smoothly and then saturates), when using PVP, which stabilizes smaller particles. At the same time the invariant shows some undulations, the most prominent of which is seen after about 100 seconds. This feature is reproducible and illuminates an interesting aspect of the reaction. It can be pulsating, where periods of nucleation are followed by periods of cluster collapse and deserves more attention. The other reactions carried out without PVP show larger particles and an even more complicated intermediate schemes, which were also present in purely optical experiments [1]. We are currently quantitatively analysing these results.

Another interesting observation is the time scale of the reaction, which is considerably faster than the lab based kinetics. When additionally comparing the growth kinetics at different x-ray exposure frequencies one finds a variable reaction speed with, however, preserved phenomenology. This shows, that the photoelectrons produced by the x-ray beam are an efficient reductant.

[1] J. Kimling, M. Maier, V. Kotaidis, B. Okenve, H. Ballot, A. Plech: *The Turkevich method for gold nanoparticles synthesis revisited* , J. Phys. Chem. B, 110 (2006) 15700.