ESRF	**Experiment title:** in situ EXAFS and SAXS of silver clusters in solution	**Experiment number**: 26-01-1044
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Report:

The objective of the experiment was to study ligand-protected Ag clusters in solution. These particles are ~1 nm in size and have earlier been found to be extremely monodisperse: as good as all clusters contain 29 Ag atoms, but the structure and shape of the clusters are unknown. We therefore recorded EXAFS and SAXS of the Ag clusters. Due to technical issues at the beamline we were unable to record EXAFS and SAXS simultaneously. Instead we recorded EXAFS first, then proceeded with SAXS.

We initially used a liquid jet setup (a closed circuit so the sample was continuously recycled), as we expected that the short exposure of the clusters to the beam would minimize radiation damage. However, this was not the case. We noticed significant changes in colour and optical properties within a few hours of measuring. When we attempted to perform the synthesis of the clusters in the liquid jet setup, the clusters did not form. Therefore we considered radiation damage to be too great to continue using the setup. Possibly the damage was caused by exposure of the sample to both to x-rays and air. Instead we prepared samples in capillaries and changed the sample often. For EXAFS, we also measured a more concentrated solution of Ag clusters to increase the signal to noise ratio.

Fig. 1 shows FT-EXAFS of concentrated Ag clusters along with a fit, giving coordination numbers of Ag-Ag = 2.9 and Ag-S = 1.3 (the ligand binds to Ag via S). This is in excellent agreement with the Ag cluster size and expected structure (a small inner Ag core surrounded by a layer containing both Ag and S). Also shown is the SAXS pattern for Ag clusters (non-concentrated). The slope suggests an elongated structure.

We also studied the synthesis in more detail, by taking aliquots in capillaries and recording EXAFS (Fig. 2). As the synthesis takes only a few hours, the number of scans per aliquot is necessarily limited and so the data are relatively noisy. However, it appears that larger particles (higher Ag-Ag and lower Ag-S coordination numbers) are present earlier in the synthesis and that these are etched into the small clusters over time.

Finally, we studied bleached (old) clusters (Fig. 3). Over time, the characteristic optical properties of the Ag29 clusters are lost. From our EXAFS data it is clear that this coincides with a reduction in Ag-Ag coordination number, thus a decrease in average size. The bleached clusters could be Ag-ligand complexes.

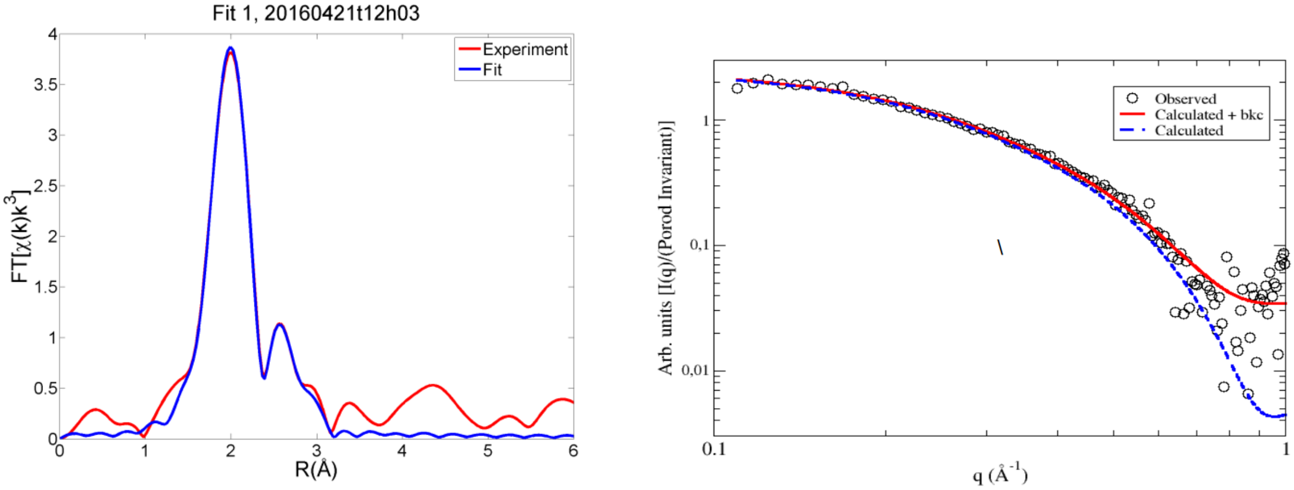

Fig. 1. FT-EXAFS (left) and SAXS (right) of Ag clusters. The SAXS pattern suggests an elongated (ellipsoid) structure, while the FT-EXAFS shows Ag-S and Ag-Ag coordination shells (at around R = 1.8 and 2.6 Å, respectively), consistent with the small size and large surface-to-volume ratio of the cluster.

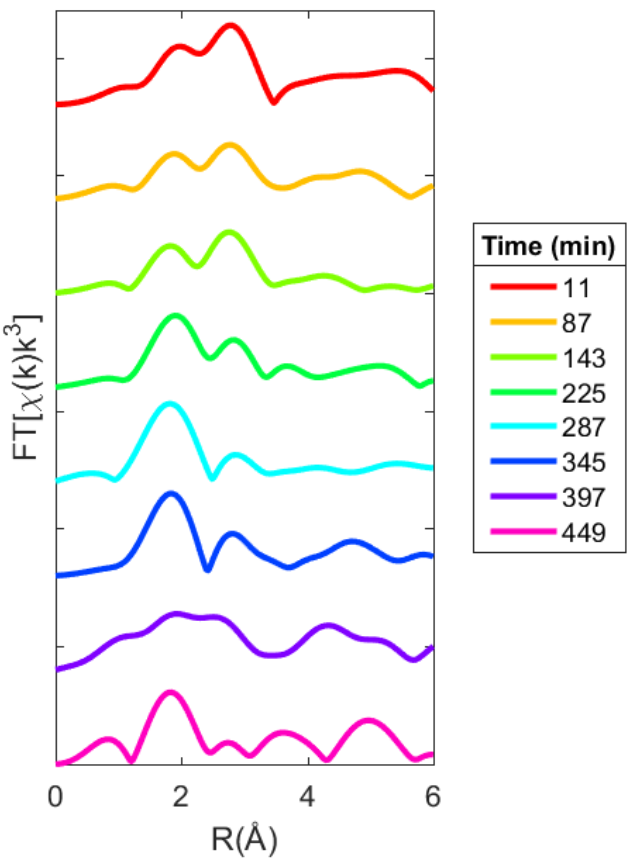

Fig. 2. FT-EXAFS of Ag clusters during synthesis. Time refers to the time since the start of the synthesis. The intensity of the Ag-Ag coordination shell (around R=2.6 Å) decreases over time, indicating a decrease in average size.

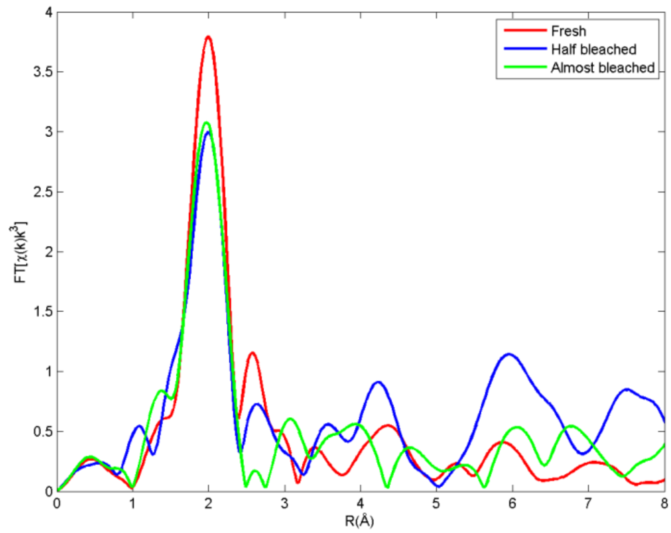

Fig. 3. FT-EXAFS of fresh clusters, half bleached clusters and almost fully bleached clusters. Ag-Ag coordination is almost completely lost for the last sample.