ESRF

ESRF	**Experiment title:** XANES and EXAFS study of lipoic acid protected gold nanoclusters	**Experiment number**: CH4593
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Report:

Background information

We studied ligand protected Au nanoclusters (~1 nm) in aqueous solution. These clusters are prepared in a two-step process in solution: 1) mixing of a gold precursor, $HAuCl_4$, with thiolate ligands, 2) addition of reducing agent to form clusters. The solution that is made after the first step is termed the synthesis intermediate. It was found that cluster size could tuned by varying the NaOH concentration (pH) during synthesis. We study three different NaOH concentrations: 8.9, 12 and 89 mM. The samples with 8.9 and 12 mM could easily be studied with laboratory techniques (mass spectrometry) to determine the size. Both samples were polydisperse (2-28 Au atoms) but average size decreased with increasing NaOH concentration. The sample with highest NaOH concentration, 89 mM, was more challenging to study with mass spectrometry but overall our analysis suggests it is in the same size regime as the other two samples.

One of our aims during this experiment was to find out during which step of the synthesis the cluster size is determined, by investigating whether the differences in cluster sizes are also reflected in different compositions/properties of the synthesis intermediates. In addition, we wanted to gain more information about the composition of the 89 mM NaOH sample.

We recorded Au L3-edge i) XANES and ii) EXAFS of Au clusters and synthesis intermediates for the three NaOH concentrations. A liquid jet setup was used to limit the radiation damage to the samples.

i) XANES of cluster solutions and synthesis intermediates

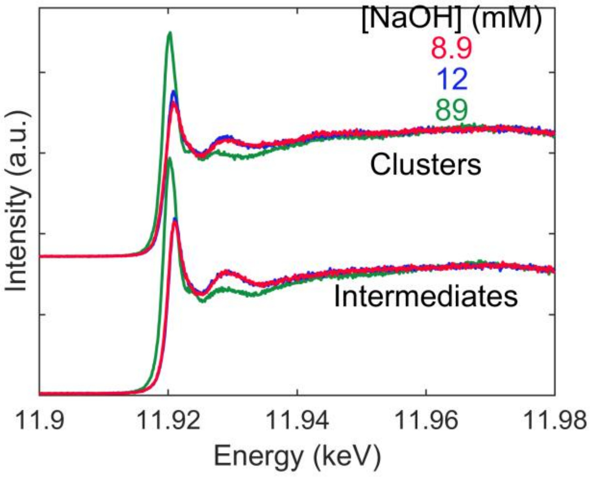
High resolution XANES spectra were recorded of all cluster samples and intermediates. We also recorded XANES of a number of reference compounds, such as Au powder, $HAuCl_4$ (a Au^{3+} compound that is the precursor for the synthesis) and sodium aurothiomalate (an Au^{+} thiolate, the ligands of the cluster are also thiolate).

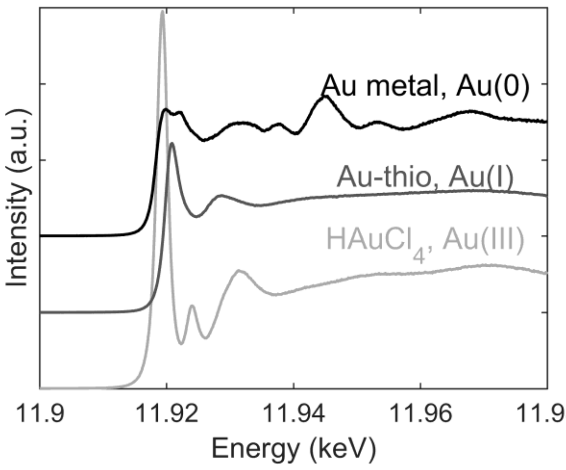
Spectra are shown in Fig. 1. It can be clearly seen that there are differences between the three cluster samples, and that these differences are already reflected in the synthesis intermediates. This is strong evidence that the synthesis intermediates have different compositions which, upon reduction, gives rise to Au clusters with different sizes. Most striking is the difference in intensity of the first feature (the whiteline). The whiteline intensity reflects the number of 5d holes which in Au can be formed by oxidation or withdrawing of electrons from Au to form bonds to ligands. A small cluster has a large surface-to-volume ratio which means it has relatively many Au-ligand and few Au-Au bonds. This in turn gives small clusters a larger number of 5d holes than large clusters and so a more intense whiteline.

For all three NaOH concentrations, we see a decrease in whiteline intensity upon going from the synthesis intermediate to the cluster, which is consistent with the reaction of synthesis intermediate with a reducing agent. However, the whiteline is still present for all clusters, and we also do not observe the spectral features that are characteristic for Au metal. This confirms the extremely small size of the clusters.

Going from 8.9 mM to 12 mM NaOH, the whiteline of the clusters increases which is consistent with a decrease in cluster size as found with mass spectrometry. The 8.9 and 12 mM NaOH cluster samples show great similarities with the sodium aurothiomalate reference (except for a lower whiteline intensity). The 89 mM NaOH cluster sample has a more intense whiteline which can reflect an even smaller average cluster size and/or partial oxidation. The 89 mM NaOH sample has some different features (a shoulder just above the whiteline) that are more consistent with $HAuCl_4$ which could indicate that not all Au is present in clusters but that some synthesis precursor remains unreacted.

The synthesis intermediates for 8.9 and 12 mM NaOH samples are nearly identical. Clearly, NaOH can also tune the cluster size in the second step of the reaction, during reduction of the synthesis intermediate.





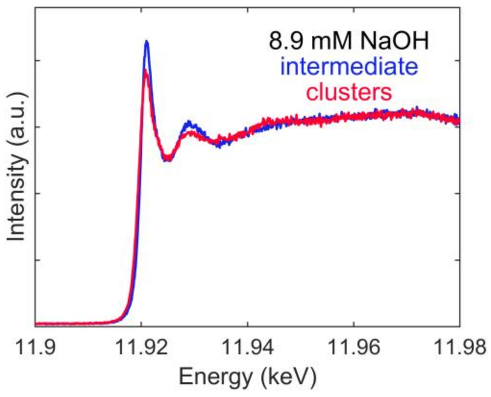


Fig 1. Top left: Au L3-edge XANES of Au clusters (top) and synthesis intermediates (bottom) for three different NaOH concentrations. Top right: XANES of three reference compounds Au metal, sodium aurothiomalate (Au-thio) and $HAuCl_4$, the precursor for the synthesis. Left: Au L3-edge XANES of cluster and synthesis intermediate compared for the 8.9 mM NaOH sample. The other two cluster samples show the same trend.

ii) EXAFS of Au clusters

EXAFS data of the three cluster samples are shown in Fig 2 together with EXAFS of references Au powder and sodium aurothiomalate. The first coordination shell of Au is clearly S, which is in good agreement with XANES. However, no clear second coordination shell is observed indicating Au-Au bonding. Calculations of Au-Au and Au-S scattering paths were done in FEFF 10.0 and fitted to the experimental data.

Au-S coordination numbers were determined to be ~3 for 8.9 and 12 mM NaOH samples and ~4 for 89 mM NaOH sample, while inclusion of a Au-Au scattering path did not improve the fit. A possible reason for the absence of clear Au-Au bonding could be because the clusters are very disordered, and/or are smaller than determined with mass spectrometry.

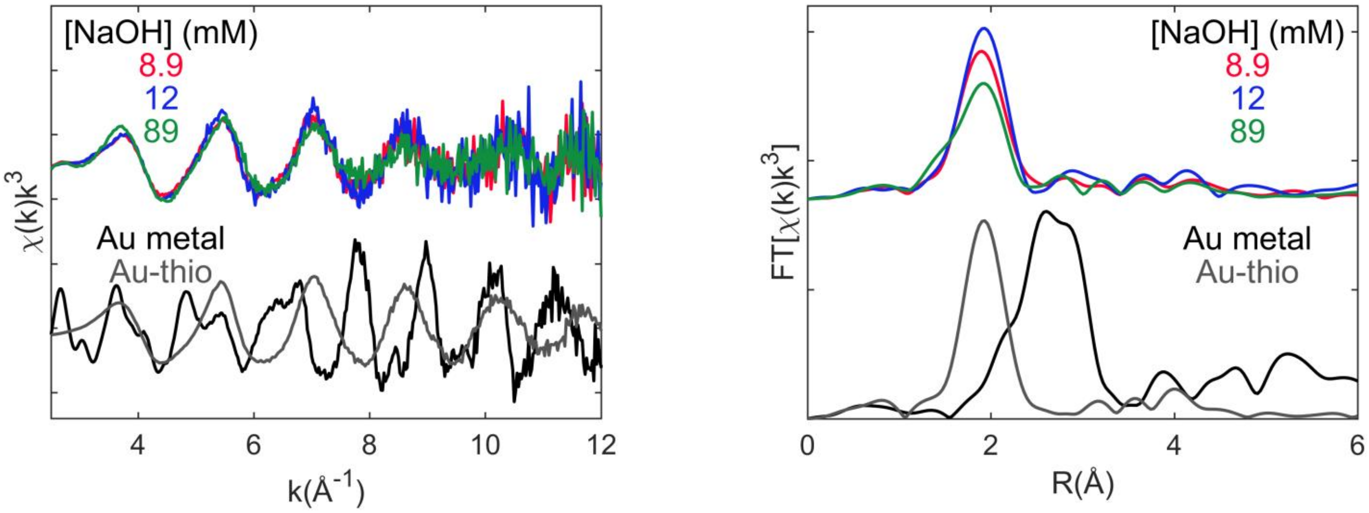


Fig. 2: EXAFS (left in k-space, right in FT-space) of the clusters with three different NaOH concentrations. Spectra of Au metal and sodium aurothiomalate (Au-thio) are shown for comparison.

Conclusions and outlook

We have recorded HERFD-XANES and EXAFS of Au clusters in solution. Cluster samples with different NaOH concentrations are seen to have different XANES, which from laboratory characterisation is related to differences in cluster sizes. It appears that there are two regimes: i) low NaOH concentration (8.9-12 mm), where the composition of the synthesis intermediate does not depend greatly on NaOH concentration and any differences between samples are due to the second reaction step, and ii) high NaOH concentration (89 mM) where the NaOH appears to inhibit complete reaction of the precursor.

As we were unable to observe Au-Au bonding from EXAFS, the question remains whether these clusters are actually particles with a compact, well-defined Au core, or if they should be considered as loose aggregates of Au-ligand complexes. We are currently performing calculations (FEFF) of XANES of a number of Au compounds in order to better understand the spectra.