

ESRF	Experiment title: XANES of Ag clusters with enhanced luminescence			Experiment number: CH4969
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Report:

Background information

We studied ligand protected Ag nanoclusters (~1 nm) in aqueous solution. These clusters are prepared in a simple one-pot synthesis: addition of a AgNO₃ solution to ligand solution, followed by addition of NaBH₄ to reduce and form clusters. The process takes ~6 hours and yields atomically monodisperse, luminescent clusters with 29 Ag atoms.

Our primary aim during this experiment were to investigate the formation of these Ag clusters. In addition, were interested in changes in the electronic structure of the Ag clusters upon addition of polymers such as poly(ethylene glycol), PEG. Addition of PEG to clusters increases the luminescence intensity, but the reason for this is not fully known yet.

We recorded Ag L₃-edge XANES of Ag₂₉ clusters during synthesis, and with/without addition of PEG. A liquid jet setup was used to limit the radiation damage to the samples. The jet was run in a He chamber to avoid attenuation of X-rays in air.

Results

Our original aim was to record XANES in situ during the synthesis. However, we found that the synthesis protocol did not work in our setup (due to X-ray radiation damage and/or the He atmosphere). However, we were able to prepare samples in the lab and put these in the jet setup at various times after the addition of the

reducing agent, thus probing ex situ the composition of the samples at various time after synthesis start. The main results are summarised in Fig. 1:

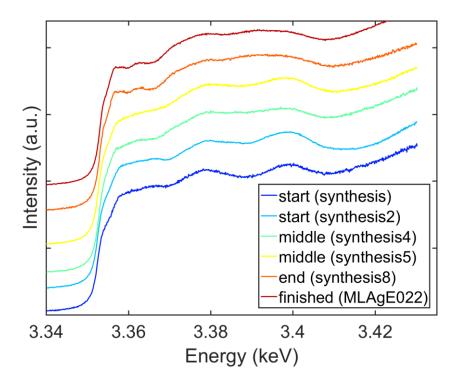


Figure 1: XANES of Ag clusters solution during synthesis. Time after addition of reducing agent increases from bottom to top.

Over time, absorption features at 3.38 and 3.40 keV become less pronounced, which may indicate increased disorder. In addition, features just above the edge become more prominent as the clusters form. We are currently performing calculations (FEFF) of XANES of a number of Ag compounds in order to better understand the spectra.