From silver ions to atomically monodisperse Ag_{29} clusters

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Noble metal clusters of ~2-100 atoms (≲1 nm) represent the missing link between plasmonic nanoparticles on the one hand and atoms/organometallic complexes on the other. The small number of atoms in clusters and thus lack of long-range order leads to discrete energy levels and unique properties not seen in larger nanoparticles, such as strong visible luminescence which is of great interest for many potential applications in sensing and biomedical imaging.[1] The properties of such clusters depend greatly on the particle size and shape. This leads to certain sizes being significantly more stable than others, meaning some sizes of clusters can be obtained with atomic monodispersity, i.e. they have a definite chemical formula rather than an average size. Investigations into the synthesis of atomically monodisperse clusters could shed important light on the mechanisms of their formation and potentially open routes to synthesise new sizes with different properties.

We present a straightforward one-pot synthesis of luminescent Ag clusters protected by the bidentate ligand lipoic acid. These clusters were found to have a size of exactly 29 Ag atoms and 12 ligands without any additional purification. The formation of the clusters was investigated by recording Ag K-edge Extended X-ray Absorption Fine Structure (EXAFS) during the synthesis. This was done directly without any sample purification or concentration that could influence the composition of the sample. Experiments were done at beamline BM26-A of the ESRF. Additional Ag L-edge X-ray Absorption Near Edge Structure (XANES) spectra were recorded at beamline ID26 of the ESRF.

EXAFS revealed average Ag-Ag coordination numbers and thus average particle size at each stage of the synthesis. Due to low Ag concentration in the samples, spectra are noisy and the k-range is short. Nevertheless, a clear trend is observed of Ag-Ag coordination number during synthesis. Our results find that initially, silver nanoparticles are formed with Ag-Ag coordination numbers of ~10; significantly larger than 29 atoms. These nanoparticles then gradually decrease in size until the Ag_{29} clusters are obtained. Further confirmation from this comes from Ag L-edge XANES where the initially pronounced features broaden over time, indicating a decrease in particle size[2]. The decrease in size may be due to etching with excess ligands present in the synthesis solution.

Ag_{29} clusters are formed via a mechanism involving a rapid initial growth followed by a size-focussing process which leaves only Ag_{29}. Our results also imply that Ag_{29} is by far the most stable size under the synthesis conditions.

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