Investigating the Influence of Solvent Protocols in Ultra-Dilute Colloidal Au: A XAFS Study.

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[Background]

Metal nanoparticle (NP) synthesis by sol-immbolisation has become increasingly popular in recent years, affording greater control of metal NP size with a narrower size distribution. Tailoring NP characteristics is desirable in the field of catalysis as it can enable the production of catalysts at lower costs with greater activity. In recent years, the ability to observe the *in situ* reduction of precursor atomic species has been noted as time-resolved X-ray absorption studies, ($M^{n+} \rightarrow M^0$). Notably, the *in situ* reduction of Au^{3+}species to Au^0 has been observed through decreases in the white line peak at 11920 eV, < 200 ms. Whilst reduction processes have been initially studied, measurement of physical NP structure by extended X-ray absorption fine-structure (EXAFS) has not been widely reported, owing to difficulties in measuring both small particle sizes (<2 nm) and at the typical concentrations used in synthesis, 100 μM. Through the use state-of-the-art modern beamlines, we detail the accurate structural information of nano-sized colloidal Au NPs obtained through EXAFS measurements at μM concentrations. Detailing the influence of Au concentration and temperature of synthesis on NP size.

[Experimental Methods]

Au NPs were synthesised through standard sol-immbolisation; $HAuCl_4$ solutions were initially prepared at various concentrations of Au: 50, 100 and 1000 μM at 1°C and capped using a solution of PVA (PVA/Au (wt/wt =0.65)). Further study of the 100 μM concentration at 25,50 and 75°C was also performed. Reduction of the sample occurred through slow addition of a $NaBH_4$ solution ($NaBH_4$/Au (mol/mol) = 5), with subsequent loading of the colloid performed for the *ex situ* pellets. XAFS measurements were performed on the I20 insertion beamline at the Diamond Light Source, here an *in situ* flow cell was used to study the colloidal NPs. Measurements were performed in fluorescence mode using a mono crystal-cut Si(111) four-bounce monochromator and collected using a 64 element Ge detector with xpress2-readout. The time resolution was 43 min / spectrum (K_{max} = 18), 6 and 3 scans were performed for the colloid and supported NPs respectively.

[Results and discussion]

EXAFS data detailed the well discussed influence of temperature in colloidal synthesis, signified by a linear trend in $|\chi|$, with the devolution of a trend from 1°C to 25°C noticeable upon immobilization. Contrary to this, increasing the Au concentration did not lead to a clear trend in colloidal Au NP size, with loading forming a trend from 50 to 1000 μM.

Fitting of the EXAFS data however, afforded colloidal NP size calculation *via* the coordination numbers of absorbing Au atoms. The stated trends were confirmed through this with temperature increase causing average colloidal NP growth from 1 to 2.2 nm (1 to 75°C) and 0.9 to 1.1 nm (50 to 1000 μM).

[Conclusions]

From the research presented, the reported ability to study colloidal EXAFS opens a new pathway for future *in situ* experiments; not only detailing the initial nucleation of atomic metal species, but also more crucially, to study the real time growth of metallic NPs.

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