

*Poster*

**PREPARATION AND CHARACTERISATION OF THIOL- AND PHOSPHINE-FUNCTIONALIZED GOLD CLUSTERS AND NANOPARTICLES: AN X-RAY ABSORPTION SPECTROSCOPY STUDY.**

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In the research field of metal nanoparticles (NPs), diameters in the nanometre and subnanometre range are of extreme interest. In this size range, the electronic properties of NPs undergo a dramatic change from a bulk-like continuum of electronic states to a discrete set of molecule-like electronic orbital levels. Extremely demanding capacities for materials characterisation are necessary in order to develop a fundamental understanding of such complex phenomena at the nanoscale. In the present work, we show that even if electron microscopy is an essential tool to visualize NPs, there are limitations to this technique that must be considered, specially, for clusters in the subnanometre range. X-ray absorption spectroscopy (XAS), and particularly, the analysis of the near edge structure (XANES) and the study of the extended fine structure (EXAFS) are revealed as an important tool in our investigation. In the present work, the aforementioned techniques, along with UV-VIS absorption spectra, have been used in combination to characterise very small gold clusters and NPs.

Au NPs stabilised by phosphine ligands which nominally contain an average number of 101 gold atoms per particle (Au<sub>101</sub>-TPP sample), have been synthesised following a modification of the Brust method [1] as proposed by Weare [2]. The exchange of the phosphine with thiol ligands [3] leads to thiolated NPs with an average number of 180 gold atoms per particle (Au<sub>180</sub>-SR sample).

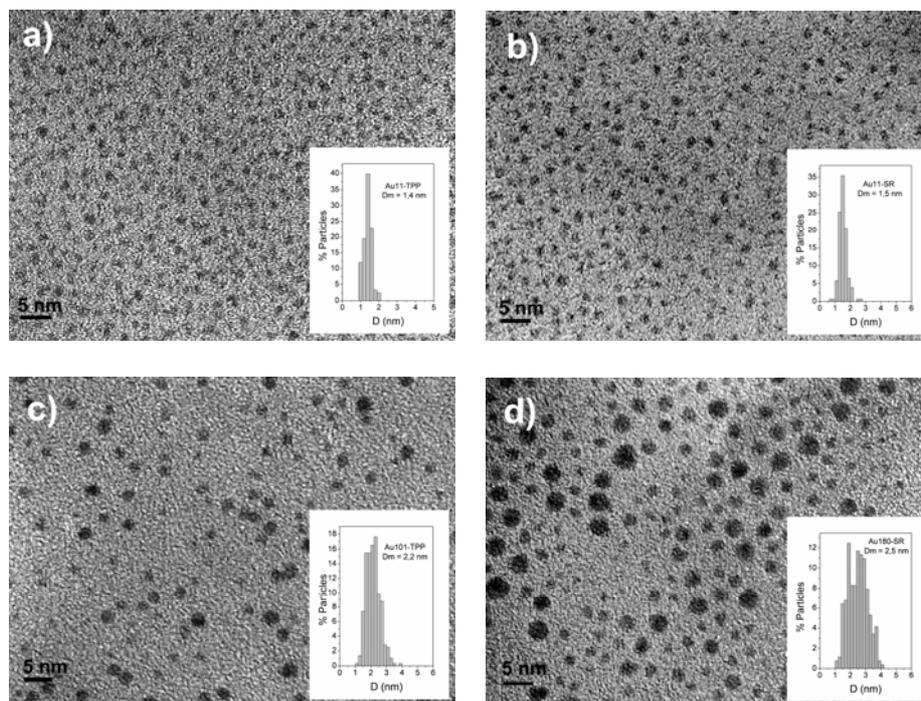
In addition, smaller gold clusters (nominally 11 gold atoms in the core) were synthesized and stabilised with the same capping molecules previously used. In this case, the starting point was a precursor molecule AuCl(PPh<sub>3</sub>) which was synthesized following the procedure described in [4]. This precursor lead to clusters capped with phosphine molecules (Au<sub>11</sub>-TPP sample) as described by Woehrle [5], which also explains the formation of thiol capped Au<sub>11</sub> NPs (Au<sub>11</sub>-SR sample) by exchange reaction of phosphine with the thiol ligands.

Both sets of NPs were then characterised using TEM (Fig. 1) in order to determine their size distribution. The TEM technique showed some difficulties when it comes to determine the size of subnanometre gold clusters such as the Au<sub>11</sub> NPs. The XAS analysis (Fig. 2a) did help to determine the bond distribution which for the Au<sub>11</sub> clusters has a strong component of Au-P and Au-S bonds compared to the dominant component of Au-Au bonds in the Au<sub>101</sub> and Au<sub>180</sub> NPs. In addition, the UV-VIS spectra in Fig. 2b showed the difference in electronic structure between the Au<sub>180</sub> and the Au<sub>11</sub> thiol capped clusters; the Au<sub>11</sub>-SR NPs have an absorption peak around 416 eV observed in the pre-exchanged particles as well (Au<sub>11</sub>-TPP). For the Au<sub>11</sub> thiol protected NPs, there is also an extra absorption feature at 676 nm which is equivalent to the transition observed in semiconductor quantum dots [6] and reflects the band gap of the NPs.

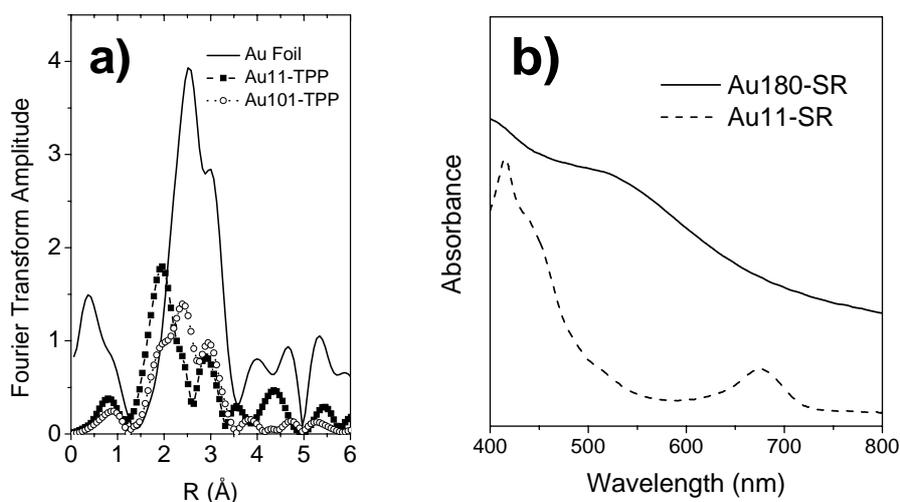
The Brust method has been proved unsuccessful to synthesize subnanometre metallic clusters, which can be easily obtained from a phosphine precursor. The XAS analysis also showed the importance of the elimination of polymer like phases during the synthesis of this very small gold clusters. These clusters have electronic properties far from the metallic behaviour found in the Au<sub>101</sub> and Au<sub>180</sub> NPs.

**References:**

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**Figures:**

**Figure 1.** TEM micrograph and particle size distribution histogram of (a) phosphine-functionalized gold clusters, Au<sub>11</sub>-TPP (b) thiol-functionalized gold clusters, Au<sub>11</sub>-SR (c) phosphine-functionalized gold nanoparticles, Au<sub>101</sub>-TPP and (d) thiolated gold nanoparticles, Au<sub>180</sub>-SR.



**Figure 2.** (a) Modulus of the Fourier Transform of EXAFS oscillations at the Au L<sub>3</sub>-edge for the phosphine-functionalized gold clusters, Au<sub>11</sub>-TPP and gold nanoparticles Au<sub>101</sub>-TPP. (b) UV-VIS absorption spectra for the thiol-functionalized gold clusters, Au<sub>11</sub>-SR and gold nanoparticles Au<sub>180</sub>-SR.