Structural Characterization of Supported Metal Nanoparticles

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This project involves the characterization of metal nanoparticles with the goal of achieving a fundamental understanding of their structural habits and the corresponding energetic landscapes. To achieve this goal, we are pursuing a combined experimental effort, utilizing advanced electron microscopy methods and X-ray absorption spectroscopy, with theoretical simulations. The systems studied include ligand-protected metal nanoparticles. Specifically, small, monodisperse Au nanoclusters, e.g. Au_{13}, have been prepared via a ligand exchange reaction of alkanethiols onto phosphine-halide gold clusters. In one synthetic protocol, two fractions separated with column chromatography exhibit very different UV-visible spectroscopy (Figure 1).

The majority fraction of these exchange products showed narrow bands in the UV-visible spectroscopy – a characteristic of a so-called "molecule-like" electronic structure. The minority fraction showed no bands in the UV-visible spectroscopy but instead exhibited an absorbance profile that increases smoothly into the UV region of the spectrum. Transmission electron microscopy (TEM) identified the majority fraction, with "molecule-like" UV visible spectrum, as sub-nanometer, highly monodisperse nanoparticles, with a very narrow size distribution, i.e., from 0.5 to 1.4 nm (Figure 2). As indicated in the histogram of the nanoparticle sizes (Fig. 2, inset), the average diameter of the Au nanoparticles is 0.81±0.19 nm. The size of the nanoparticles suggests that the typical particle of gold contains 13-55 atoms. For the minority fraction with the smoother UV visible spectroscopy, TEM revealed larger particles with an average diameter of 1.5nm.

Extended x-ray absorption fine structure (EXAFS) measurements of these two materials revealed two different structures of the Au nanoparticles (Fig. 1). The nanoparticles exhibiting a molecule-like UV-visible spectrum were found to be icosahedral. The nanoparticles with a smoothly varying UV-visible absorption spectrum was determined to be a cuboctahedral. High-resolution electron microscopy (HREM), quantitative Z-contrast and electron microdiffraction techniques are used to clarify and confirm the nanoparticle structures for individual nanoparticles in comparison to that obtained at the level of the ensemble using X-ray spectroscopies.
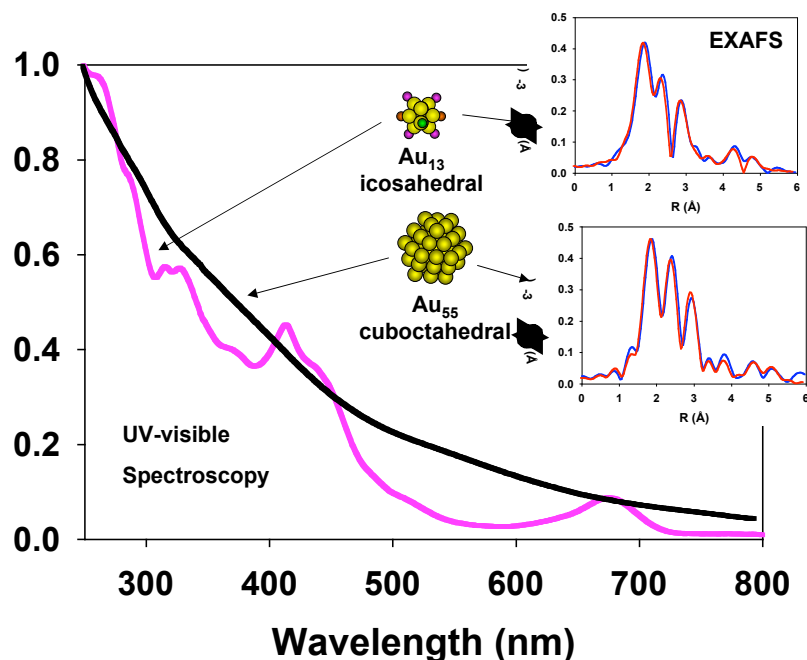
Figure 1: Two samples of Au_{13} exhibit very different UV-visible spectroscopy. EXAFS revealed that the sample exhibiting a molecule-like UV-visible spectrum (pink) was consistent with an icosahedral structure while the sample with a smoothly varying UV-visible absorption spectrum (black) was cuboctahedral . EXAFS data are shown in blue, theoretical fits – in red.
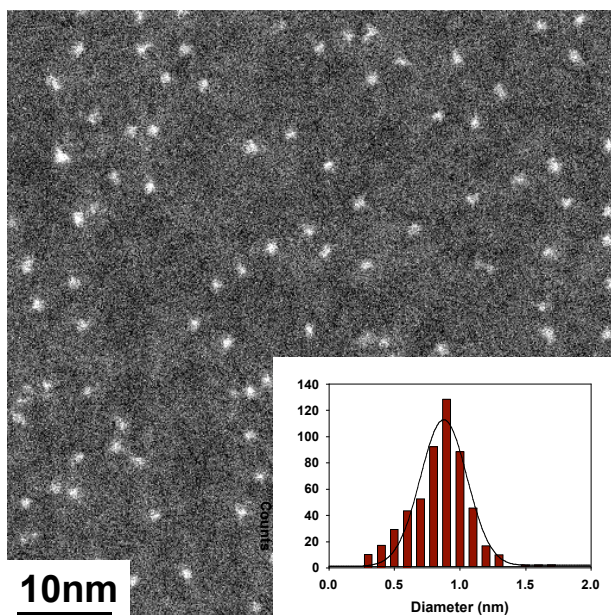
Figure 2: HAADF image of Au nanoparticles that showed "molecule-like" UV visible spectrum, where the average diameter is 0.82 nm (inset).