A Comparative XAFS Study of Gold-thiolate Nanoparticles and Nanoclusters

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Abstract. Thiopronin-capped gold nanoparticles and gold nanoclusters of sizes 3.0 and 1.5 nm, respectively, were investigated with XAFS at the gold L₃-edge. The specific EXAFS fitting procedure is discussed for obtaining reliable fit parameters for each system. The difficulties and challenges faced when analysing EXAFS data for gold nanoparticles and nanoclusters are also mentioned. Fitting results for gold nanoparticles reveal a small amount of surface Au-thiolate interactions with a large Au-Au metal core. For gold nanoclusters, only a one-shell fit was obtainable. Instead of Au-Au metal core, long-range interactions are expected for gold nanoclusters. Thiopronin-capped gold nanoclusters are proposed to be polymeric in nature, which helps explain the observed red luminescence.

1. Introduction

X-ray absorption of fine structure (XAFS) has been a technique used to aid and supplement the characterization of thiol-capped gold nanoparticles (Au NPs) [1–3]. More recently, XAFS has also become an important tool for understanding the structural environment of novel gold nanoclusters (Au NCs) where other characterization techniques are unable to provide information on the gold local structure [4,5]. Utilizing XAFS for studying Au NCs has been successful in detecting changes in structure due to cluster size and ligand environment [6,7]. Although the XAFS technique is very sensitive for identifying small structural changes, there are still many challenges researchers face when working with Au NP and NC XAFS data.

This study will focus on the XAFS analysis (near-edge and extended x-ray absorption of fine structure (EXAFS)) of thiopronin-capped (thiol-capped) Au NPs and NCs with nominal sizes of 3.0 nm and 1.5 nm, respectively. Comparing these two samples will illustrate the dramatic transition in gold structure from nanoparticles to nanoclusters as seen from XAFS results. The smaller thiopronin-capped Au NC studied here has been shown to have luminescent properties, therefore a short discussion will be included to comment on thiopronin-capped Au NC optical properties.

2. Experimental Methods

Thiopronin-capped Au NPs and NCs were synthesized following a standard colloidal preparation method [8] with additional characterization published earlier [9]. XAFS data for thiopronin-capped Au NPs and Au NCs were collected at the Advanced Photon Source (APS), operating at 6.9 GeV, in Argonne National Laboratory (ANL). Dried powder of each sample was packed and sealed in a kapton pouch for solid-state measurements. The Au L₃-edge XAFS signal was measured in transmission mode at room temperature and atmospheric pressure. EXAFS fitting was performed with the WinXAS 3.1 software package along with theoretical simulations from the FEFF8.2 computational program. The crystal structure of thiol-capped Au₂₅ nanocluster was constructed to perform FEFF calculations.
for obtaining theoretical scattering paths used in the EXAFS fitting. Specific fitting procedures are discussed in the following section as they pertain to each sample.

3. Results and Discussion

3.1 Technical EXAFS fitting results and discussion

The raw data are presented in k-space for Au foil, Au NPs, and Au NCs in figure 1. A k¹-weighting was used to compare the EXAFS oscillations between samples. The frequency of oscillations is similar for Au foil and Au NPs, indicating the Au NPs measured retain the Au fcc structure. Au NCs display an EXAFS oscillation pattern considerably different from that of Au foil and Au NPs. XAFS data quality was good for Au foil and Au NPs with a k-range up to 13.5 Å⁻¹. The data quality for Au NCs was slightly poorer with a usable k-range only up to 11.5 Å⁻¹. This was due to monochromator glitches in the high k-region of the EXAFS oscillation. Before beginning EXAFS refinements, the reduction factor (S₀²) was determined by fixing a CN of 12 for Au foil while running all other parameters free. This was done for both k¹- and k³-weighting, obtaining values of 0.81 and 0.90, respectively. Error bars in the EXAFS fits (table 1) were determined using the double residual method [1].

![Figure 1. k¹-weighted k-space of Au Foil, Au NPs, and Au NCs.](image)

3.1.1 Tiopronin-capped Au NPs

Fourier-transformed (FT) EXAFS for 3.0 nm Au NPs was transformed using a k-range of 3.3 – 11.8 Å⁻¹ and a k¹-weighting. As seen in figure 2, there is a large contribution from Au – Au bonding with a maximum at approximately 2.5 Å, not phase corrected. With a qualitative observation, Au – S contribution appears to be weak. To begin the fitting procedure for Au NPs, a preliminary fit was first done for the larger shell (Au – Au), obtaining one-shell refinement results shown in table 1. The bond length is the most reliable parameter to carry over for two-shell fitting, reducing the number of free running parameters ((# free running parameters)/2 ≤ # independent parameters is desirable). A k¹-
weighting was chosen for Au NPs to enhance low k-range features and fit the Au – S contribution. For an optimal two-shell fit, a Au – Au distance of 2.85 Å and a reduction factor of 0.81 were fixed with $E_0$ values correlated for both shells. By adjusting these parameters for the fitting procedure, we were able to reduce the number of free running parameters to obtain a reliable fit for both shells, seen in figure 2a.

From the two-shell fitting, the Au – Au CN changes from 9.7 to 9.1 once the Au – S is included in the fitting. A similar Debye-Waller value ($\sigma^2$) is found for both one-shell and two-shells. The Au – S bond length for these Au NPs is 2.46 Å. As seen from the Au – S fit in figure 2b, the amount of Au – S is very small due to the large size of the Au core. A CN value of 0.12 was determined from our fitting, which is reaching the lower limit for a reliable CN result. If the Au core were any larger for this system, Au – S contributions would most likely be unattainable. This can be a problem when using EXAFS to determine the nature of the interactions between capping ligand and surface Au when the averaged EXAFS signal for Au is heavily weighted for the metallic core.

### Table 1. EXAFS fitting results for Au Foil, Au NPs, and Au NCs.

| Bond                  | CN     | R (Å)  | $\sigma^2$ (Å$^2$) | $E_0$ (eV) |
|-----------------------|--------|--------|-------------------|------------|
| Au Foil               | Au-Au  | 12(f)  | 2.86(1)           | 0.0070(5)  | 0.6(5)     |
| Au NPs (one-shell)    | Au-Au  | 9.7(2) | 2.85(1)           | 0.0095(3)  | 0.9(3)     |
| Au NPs (two-shell)    | Au-S   | 0.1(1) | 2.46(9)           | 0.007(5)   | 0.3(9)     |
|                       | Au-Au  | 9.1(6) | 2.85(1)           | 0.0091(6)  | 0.3(9)     |
| Au NCs                | Au-S   | 1.7(2) | 2.30(1)           | 0.0060(8)  | -3(4)      |

![Figure 2](a) FT-EXAFS of Au NPs with experimental and fitted spectra (a). The contribution of Au-S and Au-Au shells are shown (b) underneath the fitted FT-EXAFS of Au NPs.

### 3.1.2 Tiopronin-capped Au NCs

FT-EXAFS for Au NCs is shown in figure 3 with a $k^1$-weighting and a k-range of 3.3-11.5 Å$^{-1}$ used for the transformation. Contrary to the 3.0 nm Au NP, the 1.5 nm Au NC has a very weak Au – Au shell and a much larger Au – S shell with a maximum around 2.0 Å, not phase corrected. Because of the weak Au – Au contribution, refinements with $k^3$-weighting were also attempted with identical k-range to $k^1$-weighting. A similar two-step, two-shell fitting method was attempted for Au NCs as for Au NPs.
First step included a one-shell fit of Au – S with a fixed reduction factor. A bond length of 2.30 Å was carried over to two-shell fitting. Both $k^1$- and $k^3$- weightings were used for fitting Au NCs. For the two-shell fitting, Au – S bond length and reduction factor were fixed with correlated $E_0$ values for both shells. Unlike Au NPs, there is a large amount of disorder in the Au – Au shell, resulting in high Debye-Waller values ($\sigma^2 > 0.05 \text{ Å}^2$). When $\sigma^2$ values were correlated for both shells, the CN values for Au – Au were unreasonably high. Correlating both $E_0$ and $\sigma^2$ obtained CN < 0.5 for Au – Au. All fitting attempts (with both k-weightings) to incorporate the Au – Au shell produced varying bond lengths ranging from 2.9-3.2 Å. From our results, we concluded that a two-shell fitting of the prepared Au NCs was inconclusive. For this reason, only a one-shell fit was reported in table 1 with $k^1$-weighting for comparison to Au NPs. The difference in Au – S bond lengths obtained from Au NPs (2.46 Å) and Au NCs (2.30 Å) could be explained by the difference in surface capping interactions. The longer Au – S bond length for Au NPs also has a significantly larger margin of error (table 1) than Au NCs due to the small contribution in the EXAFS fit (figure 2b).

A number of factors affect the refinement results for Au – Au fitting for Au NCs. Since the shell is weak, it is sensitive to the chosen k-range and k-weighting. The quality of the data hindered our fitting result because we could not use a higher k-range to confirm the nature of Au – Au bonding. This is a challenge for fitting other Au NC systems where the Au – Au environment can have multiple shells, as seen with thiol-capped Au$_{25}$ [6,7]. In the case of small cluster sizes, purity is crucial for obtaining high quality data for multi-shell Au – Au fitting.

![FT-EXAFS of Au NCs with experimental and fitted spectra.](image)

**Figure 3.** FT-EXAFS of Au NCs with experimental and fitted spectra.

### 3.2 Tiopronin-capped Au NC optical properties

From our refinement results for Au NCs, we believe the absence of a Au core and low CN values for Au – Au interactions indicates possible polymeric character of S(R)-Au-S(R) units with long-range Au – Au bonding. We believe the lack of Au core and presence of longer Au-Au contacts is responsible for the absence of a SPR band and luminescence behaviour, as seen in the previous work [9], based on the availability of discrete electronic transitions in smaller cluster sizes [10].

The near-edge spectra for Au foil, Au NPs, and Au NCs, shown in figure 4, illustrates the difference in d-electron occupancy for each sample. Au NPs and Au Foil have similar near-edge features, in
agreement with our EXAFS results. There is a shift in higher energy for both Au NPs and Au NCs relative to the foil, with Au NCs having higher edge energy. The white line intensity compliments this trend, as Au NCs appear to have more Au$^+$ character than Au NPs and Au Foil. The difference in valence state and near-edge features supports the proposed polymeric character of these Au NCs. With a higher Au$^+$ composition, Au – Au interactions are expected to be long-range and varied [11,12]. These sorts of interactions are seen in numerous Au$^+$-thiol complexes where luminescence is observed [13,14].

![Near-edge spectra comparison of Au Foil, Au NPs, and Au NCs.](image)

**Figure 4.** Near-edge spectra comparison of Au Foil, Au NPs, and Au NCs.

4. Conclusion

XAFS analysis was used to compare the structural environment of tiopronin-capped Au NPs and NCs. Au NPs were easily fit for both Au – Au and Au – S parameters where Au NCs only had reliable fitting for Au – S bonding. Even though Au – S contribution was very little for Au NPs, using a k$^1$-weighting produced reliable fitting results. Due to limited k-range and data quality, Au – Au bonding for Au NCs was unsuccessful, even with k$^3$-weighting. From our XAFS measurements, Au NCs appear to mainly consist of polymeric character with little to no metallic core. Fitting long-range Au-Au bonding was inconclusive due to the varied bond length results when EXAFS fitting conditions were changed. We conclude from this work that fitting procedures for nanoparticles and nanoclusters require certain conditions and procedures for reliable EXAFS fitting. We also report that the higher composition of Au$^+$ and evidence of polymeric -S(R)-Au-S(R)- structure is important for understanding the luminescent properties of the smaller tiopronin-capped Au NCs.

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