XAFS study on structural order in highly monodispersed thiol-stabilized Au nanoparticles

Y Huang, W Liu, L Yang, T Huang, Y Jiang*, T Yao* and S Wei
National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

* Email: yaot@ustc.edu.cn; hanyanjy@ustc.edu.cn

Abstract. Understanding the influence of thiol on nanoparticle size and structure is essential for the fundamental and applied researches. Here, using x-ray absorption fine structure (XAFS) spectroscopy, we investigate the structural order of Au nanoparticles (NPs) in the protection of thiol ligands with different contents. We found that besides protecting Au NPs against aggregation and growth, thiolates can effectively eliminate the dangling bonds of unsaturated Au atoms, and thus increase the structural order. This work enriches our knowledge of Au-S interface interaction and guides the way towards preparing size-controllable nanoparticles with specific physical/chemical properties.

1. Introduction
Au NPs are being actively investigated because of their importance in both fundamental researches and technological applications [1-4]. Ultrastable and monodispersed Au nanoparticles have usually been prepared with the protection of thiolates [5, 6]. The interaction of Au-S interface provides a practical and effective strategy to stabilize and functionalize Au NPs. Therefore, it is of great interest to understand and control the influence of thiolates on Au NPs structure.

Recently, significant progress has been made in understanding the structure of ultrasmall (<2 nm) Au NPs [7, 8]. Despite the internal structures of Au NPs with sizes ranging from clusters to nanocrystals (2.0-4.0 nm) have been reported [9], it is not enough for scientific research, partially because of the challenges in synthesizing and crystallizing monodispersed nanoparticles. Moreover, the structural order plays an important role in determining properties of the particles. In such cases, synchrotron-based XAFS technique can provide atomic-scale structural information, including the surface bond length and structural disorder, with crystallographic resolution independent of the sample crystallinity.

Here, we report the preparation of highly monodispersed Au NPs with controllable sizes of ~2.0-4.0 nm, by adjusting the precursor to surfactant ratio in a one-pot chemical solution synthesis. Using
synchrotron-based XAFS technique as a sensitive local-structural probe, we present a detailed study on
the structural order and bond length of these Au NPs in the protection of thiol ligands.

2. Experimental Section
Preparation of dodecanethiol capped Au NPs: The 0.064 g AuCl(PPh)$_3$ was dissolved in 21 mL ethanol at
room temperature. Then dodecanethiol was added. After 5 minutes, 0.108 g C$_4$H$_{14}$BN was dissolved in
the mixture. And then the mixture was kept stirring for 10 hours. The product was collected by
centrifugation and washed with ethanol to remove the physical absorbed and residual dodecanethiol.

TEM images were obtained with a JEOL 2010 system. The UV-Vis spectra were recorded on a UV-
2501PC/2550 spectrophotometer in the wavelength range of 300–800 nm. XRD patterns were
obtained on a Rigaku X-ray diffractometer D/ MAX–2200/PC equipped with Cu Kα radiation (40 kV,
20 mA). XAFS measurements were performed at BL14W1 beamline of Shanghai Synchrotron Radiation
Facility (SSRF), using ionization chambers with optimized detecting gases in transmission mode. The
storage ring of SSRF worked at 3.5 GeV with a maximum current of 210 mA. The samples were taken
into a Telfon cell and the thickness of the cell was adjusted to reach the optimum absorption thickness.

3. Results and discussion

We used ratios (Au:S) of 1:1, 1:2, 1:4, and 1:6 yielding NPs of 3.7, 3.2, 2.3, and 1.8 nm, respectively, as
revealed by the TEM images in Figs. 1b–e. These particles are in spherical shape and have a narrow size
distribution of ~0.1-0.2 nm, indicating the high monodispersity. For the size distribution, we used
sampling methods to estimation the mean value by randomly selecting 100 particles. By decreasing the
amount of the thiol, the sizes of NPs gradually increase, indicating the importance of thiol for the
preparation of stable and monodispersed Au NPs.

Figure 1. Synthetic strategy (a), TEM images (b-e), the insets show the
corresponding size distributions. Plot of average size against Au:S ratios (f)
The UV-vis spectra shown in Fig. 2a exhibit one intense surface plasmon band peaked at 510 nm, which is originated from the characteristic plasmon resonance absorbance for spherical Au NPs larger than 2 nm. This absorbance intensifies with increasing Au:S ratios, suggesting the increased NP size. For the NPs synthesized with Au:S ratios of 1:6 and 1:4, the spectral profile is highly structured and displays the fingerprint features of small Au NPs with molecule-like electronic structure, as the sizes are on the edge of metal to semiconductor transition. In Fig. 2b four strong Bragg reflections can be seen, which correspond to the (111), (200), (220) reflections of fcc Au, showing distinct diffraction pattern, indicating better crystalline Au NPs were formed.

We plot in Figure 3a,b the EXAFS oscillation $k^2\chi(k)$ and the corresponding Fourier-transformed (FT) spectra. The atomic structures of Au NPs synthesized with different Au:S ratios vary significantly, as reflected by the obviously different EXAFS oscillation shapes. The Au–S coordination peaks at 1.9 Å significantly weaken with the increasing of Au:S ratios, implying the weakened Au-thiols interaction. While the intensity of the Au–Au coordination peaked within 2.15-2.25 Å vary interestingly. The weaker peak gradually reduced relating to the NP size, which can be inferred from the fact that the 2.3 nm and 1.8 nm NPs synthesized with Au:S ratio of 1:4 and 1:6 has the relative lower Au-Au peak than the 3.2 nm and 3.7 nm NPs. However, little evidence of variation is observable in the first stronger peak of Au-Au coordination. In XANES spectra, white-line peak (corresponding to the electronic transition from the $2p_{3/2}$ to the $5d_{5/2, 3/2}$ states) at around 11926 eV increases in intensity with increasing Au:S ratio. This corresponds to the increased Au→S d-charge transfer, consistent with the enhancement of the interaction.
between dodecanethiol and Au surfaces. We consider that the tailor of electronic performance was achieved just by control the particle size. Additionally, the variations of the intensities of Au–Au bond peak mainly come from the particle size, without the influence of structure disorder, as consistent with XRD results.

The detailed structural information evolution process could be obtained by EXAFS fitting, as played in Table 1. Quantitative least-squares curve-fitting in the R-space with a Fourier transform k-space range of 2.2–12.5 Å⁻¹ and a typical R ranges of 1.3–3.2 Å was carried out using module ARTEMIS of programs of IFEFFIT [10]. The contributions of Au atoms at the surface and in the core of a particle were separated in the fitting by defining a parameter p for the fraction of core atoms of the Au NPs. We calculate this value in accordance with the Au atom size and the particle size. The amplitude reduction factor (S₀²) was fixed at 0.86 during the fitting. With reducing the Au:S ratio from 1:1 to 1:6, the statistical factors of reduced chi-square (χ²) were 8.03, 9.42, 8.69, 7.93, and R factor were 0.0019, 0.0018, 0.0019, 0.0020, respectively. And both the surface Au–Au and Au–S coordination number (CN) gradually increased (from 5.6 to 6.4 and 0.8 to 1.3). Generally, unsaturated surface Au atoms have lots of dangling bonds, and hence more structure disorder. Interestingly, the disorder degree σ² of the surface Au–Au bonds (R) in the prepared Au NPs almost remain at about 0.009 Å². For the Au nanocrystals prepared here, S atoms would occupy the surface hollow sites with a typical tetrahedral configuration formed by three Au surface atoms and a head S atom. Hence, the dodecanethiol coverage can be estimated from the Au–S bond CN using the expression of CN_{Au,S}/3.0 [11]. The results indicate that coverage increase from 0.27 to 0.43 with reducing Au:S ratio from 1:1 to 1:6. A larger thiol coverage protect the Au NPs against aggregation and further growth, leading to a small particle size. On the other hand, more dangling bonds residual were replaced by Au–S bonds, resulting enhanced structure order.

4. Conclusion
In summary, highly monodispersed plasmonic Au NPs with controllable sizes of ~2.0-4.0 nm were prepared by adjusting the precursor to surfactant in a simple feasible synthesis. Thiolates play two roles
in the process of preparing Au NPs. First, the thiol ligands protect Au NPs against aggregation and further growth. On the other hand, the formation of Au-S bonds effectively eliminate the dangling bonds on the surface of the Au NPs, and thus increase the structure order of the nanoparticles. This work enriches our knowledge of Au-S interface interaction and guide the way towards preparing size-controllable nanoparticles with specific physical/chemical properties.

Acknowledgments

This work was supported by National Science Foundation of China (Grant No. 11175184, 11135008, 11205158, U1332131, and 11305172). The authors are grateful to SSRF for the valuable beamtime.

References

[1] Daniel M C and Astruc D 2004 Chem. Rev. 104 293.
[2] Wang L et al 2015 Nat. Commun. 6 6957.
[3] Pyo K et al 2015 J. Am. Chem. Soc. 137 8244.
[4] Yoshida H et al 2012 Science 335 317.
[5] Yin Y and Alivisatos A P 2005 Nature 437 664.
[6] Vericat C et al 2010 Chem. Soc. Rev. 39 1805.
[7] Yao T et al 2010 J. Am. Chem. Soc. 132 7696.
[8] Li Y Y et al 2012 J. Am. Chem. Soc. 134 17997.
[9] Chevrier D M et al 2013 J. Phys.: Conf. Ser. 430 012029.
[10] Ravel B and Newville M 2005 J. Synchrotron Rad. 12 537.
[11] Jiang Y et al 2012 J. Phys, Chem. C 116 24999.