XAFS studies of monodisperse Au nanoclusters formation in the etching process

Lina Yang, Ting Huang, Wei Liu, Jie Bao, Yuanyuan Huang, Yuanjie Cao, Tao Yao, Zhihu Sun*, and Shiqiang Wei*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

Corresponding authors. E-mail: zhsun@ustc.edu.cn, sqwei@ustc.edu.cn

Abstract. Understanding the formation mechanism of gold nanoclusters is essential to the development of their synthetic chemistry. Here, by using x-ray absorption fine-structure (XAFS) spectroscopy, UV-Vis and MS spectra, the formation process of monodisperse Au13 nanoclusters is investigated. We find that a critical step involving the formation of smaller Au8−Au11 metastable intermediate clusters induced by the HCl + HSR etching of the polydisperse Au_n precursor clusters occurs firstly. Then these intermediate species undergo a size-growth to Au13 cores, followed by a slow structure rearrangement to reach the final stable structure. This work enriches the understanding of cluster formation chemistry and may guide the way towards the design and the controllable synthesis of nanoclusters.

1. Introduction

Gold nanoclusters possess size-dependent molecular-like structure and discrete electronic energy levels, which render them diverse applications in fields such as catalysis, optical devices and imaging [1-5]. Therefore, the development of synthetic strategies for monodisperse Au nanoclusters is crucial. Currently, etching polydisperse Au clusters has been widely employed as an useful top-down method and obtained remarkable advances. However, the mechanistic understanding on the etching-induced synthesis of monodisperse nanoclusters is still to be resolved [6]. Therefore, it is important to study etching reactions for developing more routes to fine-tune nanoclusters with desired functionalization.

Currently, direct liberation of the same-sized particle as the target cluster in a single step was hypothesized but not experimentally verified [7]. What happens in the convergence process and how this process is related to the structure and property of the end product is scarcely known. In order to solve these problems, in-situ methods by a combination of various probing techniques with sensibility to transient intermediate species in solution are specially required.
Herein, we report an investigation on the kinetic formation process of an unprecedented monodisperse Au\(_{13}\)(L\(_3\))(SR)\(_4\)Cl\(_4\) nanocluster (L\(_3\): 1,3-Bis(diphenylphosphino)propane) by in-situ x-ray absorption fine structure (XAFS), UV-vis absorption and MS spectra. The Au\(_{13}\) nanocluster is obtained via a facile one-phase reaction of polydisperse Au\(_n\) clusters with hydrochloric acid (HCl) and dodecanethiol (HSR). It is found that the formation of the monodisperse Au\(_{13}\)(L\(_3\))(SR)\(_4\)Cl\(_4\) nanoclusters is realized in an etching/growth/rearrangement manner including three reaction stages.

2. Experimental Section

Sample preparations: The monodisperse Au nanoclusters were synthesized by reaction of HCl and HSR mixture with preformed L\(_3\)-capped Au\(_n\) clusters. The starting material of this reaction, L\(_3\)-capped Au\(_n\) clusters, was synthesized by reduction of Au\(_2\)(L\(_3\))Cl\(_2\) (70 mg, 0.08 mmol) with NaBH\(_4\) (15 mg, 0.04 mmol) in 60 ml dichloromethane solvent at room temperature for 3 h under stirring \([6]\). The solvent was evaporated to dryness and then redissolved in 12 ml ethanol, to which a mixture of dodecanethiol (50 \(\mu\)L, 0.2 mmol) and HCl (200 \(\mu\)L, 2.4 mmol) was added. The process of the reaction was monitored by in-situ XAFS spectra, UV-Vis, as well as mass spectrometry.

In-situ XAFS measurement: The Au L\(_3\)-edge XAFS spectra were measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The storage ring of SSRF worked at 3.5 GeV with a maximum current of 210 mA. The reactive solution was continuously circulated along a microtube by peristaltic pump and flowed into an in-situ cell for XAFS measurement.

3. Results and discussion

![Figure 1](image-url)

**Figure 1.** *In situ* UV-vis absorption spectra and MALDI mass spectra at different reaction times. The inset shows the MALDI-MS of the starting material at a wide mass range.

The time-dependent UV-vis absorption and MALDI-MS spectra for the formation process of monodisperse Au\(_{13}\)(L\(_3\))(SR)\(_4\)Cl\(_4\) nanoclusters were shown in Fig. 1. At first, the UV-Vis spectrum demonstrates a wide hump at around 500 nm, suggesting the polydispersity of the precursor clusters.
At 30 min the spectral profile shows a featureless decay. From 2 h on, absorption bands peaked at 327, 410, 433, and 700 nm become gradually pronounced and reach saturation. The MS spectra for the starting material covers a wide size range of 3000–13000 Da, corresponding to a mixture of Au$_{15}$–Au$_{60}$. Within the 30 min, the wide size distribution is divided into two regions covering roughly 6000–8000 and 3000–4000 Da, which could be assigned to Au$_{31}$–Au$_{39}$ and Au$_{8}$–Au$_{11}$ clusters respectively. At 2 h, only the peaks at 4101 and 4335 Da are present. These two peaks are corresponding to Au$_{3}$(L$_{3}$)$_{2}$(SR)$_{3}$Cl$_{4}$ cluster (a fragment of and intact, respectively), indicating complete size-convergence into Au$_{13}$ clusters.

**Figure 2.** (a) Time-dependent XANES spectra, and (b) EXAFS spectra. (c) Coordination number CN, (d) bond distance $R$, and (e) Debye-Waller factor $\sigma^2$ against reaction time extracted from EXAFS curve-fitting. Au–Au(c-p) and Au–Au(p-p) represent the central-peripheral and peripheral-peripheral Au–Au bonds in a complete or incomplete icosahedron, respectively.

In situ XAFS measurements at Au $L_3$-edge were performed to detect the evolutions of the size-conversion process. The XANES spectra in Fig. 2(a) display that the spectrum of the starting material exhibits a peak at 11936 eV (labeled by an arrow), which is characteristic of fcc structured Au. After addition of HCl + HSR, the intensity of this peak is remarkably smeared out at 30 min, and disappears completely at 2h. The peak shape is similar to nanoclusters. The Fourier transformed (FT) EXAFS $k^2\chi(k)$ curves in Fig. 2(b) also show that immediately after the start of reaction (within 30 min), the Au-ligand (Au–S/P/Cl) peak at 1.90 Å is intensified rapidly, while the Au-Au peaks (2.36 and 2.88 Å) are significantly damped, suggesting the decomposition of the larger clusters. Moreover, the white-line peak at around 11926 eV in the XANES spectrum, corresponding to the $2p_{3/2}\rightarrow5d_{5/2,3/2}$
electronic transition of Au atoms, is significantly intensified immediately after the addition of HCl +
HSR. With continued reaction, the white-line peak is reduced slightly in intensity, along with the
gradually weakened Au-Au peaks in the FT curve. After 2 h, the XANES spectra do not display any
remarkable changes, while subtle continuing increase of the Au-ligand EXAFS peak intensity could be
discerned. Quantitative structural parameters have been obtained through a least-squares curve-fitting
using the ARTEMIS [8] module of IFEFFIT package. We will discuss the details in the following.

Within the first stage of 30 min, Au_{15}^{−}−Au_{60} clusters with Au-ligand CN of 0.44, are prominently
etched into smaller Au_{8}−Au_{11} metastable intermediates. Subsequently, these active small Au_{8}−Au_{11}
clusters are immediately stabilized by the absorbed SR, L₃ and Cl⁻ ligands to form metastable
intermediates as evidenced by the quickly increased Au-ligand CN (from 0.44 at 0 min to 0.72 at 30
min). These Au_{8}−Au_{11} cores are fully protected by the ligands, forming closed geometrical shells that
make the clusters highly resistant against etching. In the second stage (30 min-2 h), these metastable
Au_{8}−Au_{11} intermediates focus into Au_{13} cores, which is possibly achieved by incorporating the Au(I)
ions or Au(I)-Cl oligomers pre-existing in the solution. The obtained Au-ligand CN (1.02) at 2h is
between the nominal values in Au_{13}(L₃)₂(SR)₄Cl₄ (0.92) and Au(I)-SR polymers (2.0) [10], suggesting
the existence of both species. The proportion \(p\) of the Au atoms in Au_{13}(L₃)₂(SR)₄Cl₄ could be
estimated by the equation 0.92\(×p+2×(1−p)=1.02\), which gives \(p=0.90\). This result demonstrate that the
majority (~90%) of Au atoms at 2 h is in the form of Au_{13} cluster, with a small part (~10%) forming
Au(I)-SR polymers or analogues. In the third stage (after 2 h), the atomic structure undergoes a
rearrangement process toward the energetically stable structure. The EXAFS curve-fitting show that
during the structure rearrangement process, the Au–Au bond displays a trend of contraction. At the
beginning of forming Au_{13} skeletons, both the \(R_{Au-Au(c-p)}\) and \(R_{Au-Au(p-p)}\) (2.72 and 2.95 Å) of the Au_{13}
icosahedron are within the typical range (2.71–2.79 and 2.85–2.95 Å) of Au_{13} clusters as previously
reported [9]. After the structure rearrangement, the \(R_{Au-Au(c-p)}\) and \(R_{Au-Au(p-p)}\) decrease to 2.67 and 2.89 Å,
respectively, suggesting a considerable structural distortion away from the original icosahedral Au_{13}
skeleton. The gradually enlarged distortion is also reflected by the slightly increased disorder degree
\(σ²\) of the Au-Au bonds, from 0.015 to 0.017 Å². This implies the structural rearrangement of Au_{13}
clusters.

4. Conclusion
In summary, in-situ XAFS combined with MS and UV-Vis have been used to probe the formation
process of the monodisperse Au_{13}(L₃)₂(SR)₄Cl₄ nanocluster. It is found that the cluster formation is
achieved in an etching/growth/rearrangement manner including three distinct reaction steps. (1) The
initial polydisperse Auₙ clusters are etched to form much smaller Auₙ−Au_{11} intermediate clusters. (2)
These intermediate species undergo a size growth to Au_{13} cores, by incorporating the pre-existing Au(I)
ions or Au(I)-Cl oligomers in the solution. (3) Finally, a slow structure rearrangement of the Au_{13}
skeleton and the covering ligand shells occurs. These findings enrich our understanding on the etching
mechanism and can guide our way towards the synthesis of nanomaterials in a controllable manner.

Acknowledgments
This work was supported by National Natural Science Foundation of China (Grant No. 11475176,
11135008, U1332131, and 11305172). The authors are grateful to SSRF for the valuable beamtime.
References

[1] Jin, R. C. Nanoscale 2010, 2, 343.
[2] Li, G.; Jin, R. C. Acc. Chem. Res. 2013, 46, 1749.
[3] Qian, H. F.; Zhu, M. Z.; Wu, Z. K.; Jin, R. C. Acc. Chem. Res. 2012, 45, 1470.
[4] Yau, S. H.; Varnavski, O.; Goodson, T. Acc. Chem. Res. 2013, 46, 1506.
[5] Lu, Y. Z.; Chen, W. Chem. Soc. Rev. 2012, 41, 3594.
[6] Shichibu, Y.; Konishi, K. Small 2010, 6, 1216.
[7] Duan, H. W.; Nie, S. M. J. Am. Chem. Soc. 2007, 129, 2412.
[8] Ravel, B.; Newville, M. J. Synchrotron Rad. 2005, 12, 537.
[9] Hall, K. P.; Mingos, D. M. P. Prog. Inorg. Chem. 1984, 32, 237.
[10] Menard, L. D.; Frenkel, A. I.; Murray, R. W.; Nuzzo, R. G. J. Phys. Chem. B 2006, 110, 14564.