

Study of the structure and electronic state of thiolate-protected gold clusters by means of ^{197}Au Mössbauer spectroscopy

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Abstract We have investigated the structures and electronic states of a series of glutathionate-protected Au clusters, $\text{Au}_n(\text{SG})_m$ with $n = 10 - \sim 55$, using ^{197}Au Mössbauer spectroscopy, which allows us to probe the local environment of the constituent Au atoms via isomer shift (*IS*) and quadrupole splitting (*QS*). The spectral profile abruptly changes on going from $\text{Au}_{22}(\text{SG})_{17}$ to $\text{Au}_{25}(\text{SG})_{18}$, then it smoothly changes to that of $\text{Au}_{\sim 55}(\text{SG})_m$. However, the spectral profile dramatically changes on going from $\text{Au}_{\sim 55}(\text{SG})_m$ to the dodecanethiolate-protected Au cluster with average diameter of 2 nm. The ^{197}Au Mössbauer spectra of glutathionate-protected Au clusters and dodecanethiolate-protected Au clusters were successfully analyzed on the basis of the structure and electronic state of $\text{Au}_{25}(\text{SG})_{18}$.

Keywords Gold cluster · ^{197}Au Mössbauer spectroscopy · Nanomaterial

1 Introduction

In the last decade, small Au clusters composed of less than 100 atoms protected by organic ligands have attracted much attention as a prototypical system for fundamental studies on quantum size effect and as a building block of nano-scale

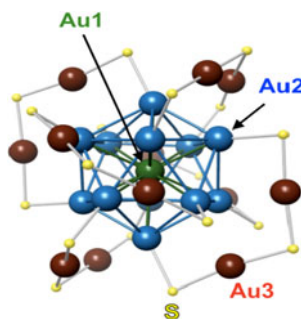
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Fig. 1 Core structure of $\text{Au}_{25}(\text{SR})_{18}$ [6, 7]. Large and small balls represent Au and S atoms, respectively. R group is omitted for simplicity



devices [1]. In connection with organic ligands, thiolates (RS) have extensively been used [2]. Among small Au clusters, the Au-thiolate compound composed of 25 Au atoms and 18 thiolates ($\text{Au}_{25}(\text{SR})_{18}$) has been studied most extensively as a prototype system of stable $\text{Au}_n(\text{SR})_m$ clusters [3]. In 2007, we proposed the structure of $\text{Au}_{25}(\text{SG})_{18}$ by ^{197}Au Mössbauer spectroscopy [4], based on the “core-in-cage” model theoretically predicted by Iwasa and Nobusada; the Au_7 core is caged by two $[\text{Au}-\text{S}(\text{R})-\text{R}]_3$ and one $[\text{Au}-\text{S}(\text{R})-\text{R}]_{12}$ cyclic oligomers [5]. Since then, the geometrical structure of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ was determined by single crystal X ray diffraction [6] and by theoretical calculation [7]. According to the structural analysis, $\text{Au}_{25}(\text{SR})_{18}$ is composed of an icosahedral Au_{13} core whose surface is protected by six staples, $-\text{S}(\text{R})-\text{[Au}-\text{S}(\text{R})-\text{R}]_2$, as shown in Fig. 1. Based on the structure of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$, we re-analyzed the ^{197}Au Mössbauer spectrum of $\text{Au}_{25}(\text{SG})_{18}$ [8]. In this paper, we have analyzed the ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ ($n = 10 - \sim 55$) and dodecanethiolate-protected Au clusters with the average diameters of 2 nm and 4 nm (here after, described as Au clusters of 2 nm and 4 nm) on the basis of the structure and electronic state of $\text{Au}_{25}(\text{SG})_{18}$.

2 Experimental

The $\text{Au}_n(\text{SG})_m$ samples with $(n, m) = (10, 10), (15, 13), (18, 14), (22, 16), (22, 17), (25, 18), (29, 20), (33, 22), (39, 24), (45, 28)$, and $(\sim 55, m)$ [9] were fractionated from nearly monodisperse Au:SG clusters ($d_{av} \sim 1$ nm) using polyacrylamide gel electrophoresis (PAGE) [3(a), 10]. In order to obtain the ^{197}Au Mössbauer spectra with sufficient S/N ratio, each cluster was accumulated up to 50–100 mg by repeating the elaborative PAGE procedure [4]. The dodecanethiolate-protected Au clusters of 2 nm and 4 nm were prepared by the direct chemisorption method and the ligand-exchange method, respectively [11]. The distribution of particle size and the diameter of dodecanethiolate-protected Au clusters were analyzed by small-angle X-ray scattering as well as transmission electron microscopy [11].

^{197}Au Mössbauer spectra were measured at the Research Reactor Institute of Kyoto University. The γ -ray source (77.3 keV), ^{197}Pt , was generated by neutron irradiation of a 98%-enriched ^{196}Pt metal foil. The γ -ray source and samples were cooled down to 16 K. The IS value of Au foil was referenced to 0 mm/s. The spectra were calibrated by using the six lines of a body-centered cubic iron foil (α -Fe). Mössbauer spectra were fitted with a MossWinn 3.0 program [12].

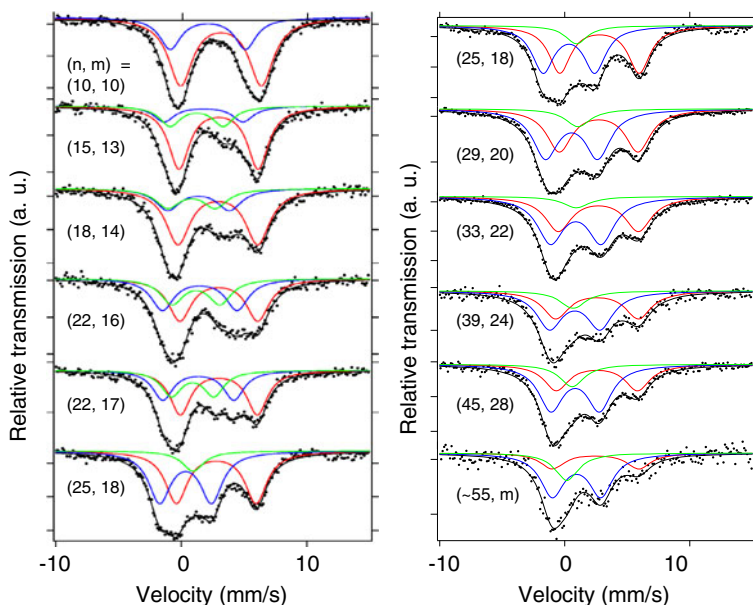
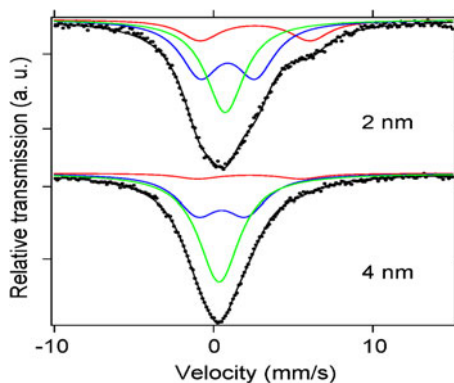


Fig. 2 ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ ($n = 10 - \sim 55$)

3 Results and discussion

The ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ with $(n, m) = (10, 10), (15, 13), (18, 14), (22, 16), (22, 17), (25, 18), (29, 20), (33, 22), (39, 24), (45, 28)$, and $(\sim 55, m)$ are shown in Fig. 2. These spectra were analyzed based on the structure of $\text{Au}_{25}(\text{SR})_{18}$ ($\text{SR} = \text{SC}_2\text{H}_4\text{Ph}$). As shown in Fig. 1, the Au atoms in $\text{Au}_{25}(\text{SR})_{18}$ are classified into three sites from the viewpoint of chemical environment; a single central Au atom of the core (**Au1**, green ball in Fig. 1), twelve Au atoms at the core surface each of which are bound by a single thiolate (**Au2**, blue ball in Fig. 1), twelve Au atoms on the outermost layer which are bound by two thiols (**Au3**, red ball in Fig. 1). These three sites should exhibit different isomer shift (IS) and quadrupole splitting (QS) values due to the difference in electronic structures of each site. On the basis of symmetry considerations, the **Au1** and **Au2/Au3** atoms presumably produce singlet ($QS = 0$) and doublet peaks, respectively. Therefore, the spectrum was fitted by the superposition of a singlet Lorentzian and two sets of doublet Lorentzians while assuming identical FWHM values for all the components. The ^{197}Au Mössbauer spectrum of $\text{Au}_{25}(\text{SR})_{18}$ in Fig. 2 is the best fitting result taking account the structure. The doublet (**c3**) with the largest IS (2.78 mm/s) and QS (6.35 mm/s) is assigned to the twelve Au atoms (**Au3**) on the outermost layer coordinated by two thiols. These Mössbauer parameters, IS and QS , are typical of Au(I) coordinated by two sulfur atoms [13]. The second doublet (**c2**) with $IS = 0.34$ mm/s and $QS = 4.14$ mm/s is assigned to the twelve Au atoms at the core surface, each of which bound by a single thiolate (**Au2**). The singlet (**c1**) with $IS = 0.94$ mm/s and $QS = 0.00$ mm/s is assigned to the central Au atom of the core (**Au1**). This assignment is consistent with the structure of $\text{Au}_{25}(\text{SR})_{18}$.

Fig. 3 ^{197}Au Mössbauer spectra for dodecanethiolate-protected Au clusters of 2 nm and 4 nm



As shown in Fig. 2, the ^{197}Au Mössbauer spectra of a series of $\text{Au}_n(\text{SG})_m$ evolve drastically as a function of the core size. Asymmetric doublet profile of the $\text{Au}_{10}(\text{SG})_{10}$ spectrum could be fitted by a superposition of two sets of doublets. The IS and QS values obtained are 3.06 and 6.68 mm/s, respectively, for the major component and 2.48 and 5.71 mm/s for the minor component. According to the correlation between the IS and QS values established for various kinds of Au(I) and Au(III) compounds, these Au atoms fall in a category of Au(I) atoms directly coordinated by two SG ligands [13]. The spectra of $\text{Au}_n(\text{SG})_m$ ($15 \leq n \leq 22$) were fitted by three sets of doublets. Two components are assigned to Au(I) coordinated by two SG ligands since the IS and QS values are smoothly correlated to those of $\text{Au}_{10}(\text{SG})_{10}$. The third component having the smallest IS and QS values is assigned to Au(I) coordinated by a single SG ligand which is smoothly correlated to those of the **Au2** atoms coordinated by a single SG ligand. The spectral profile abruptly changes on going from $\text{Au}_{22}(\text{SG})_{16}$ to $\text{Au}_{25}(\text{SG})_{18}$, in which a core Au atom (**Au1**) comes out.

On the other hand, on going from $\text{Au}_{25}(\text{SG})_{18}$ to $\text{Au}_{\sim 55}(\text{SG})_m$, the spectral profile smoothly converges to that of $\text{Au}_{\sim 55}(\text{SG})_m$. In these Au clusters, the spectrum was fitted by the superposition of a singlet Lorentzian due to core Au atoms and two sets of doublet Lorentzians due to Au atoms coordinated by a single SG ligand and two SG ligands. With increasing n , the ratio of **Au2** atoms to **Au3** atoms increases. However, the spectral profile dramatically changes on going from $\text{Au}_{\sim 55}(\text{SG})_m$ (the average diameter is estimated at about 1.4 nm) to the dodecanethiolate-protected Au cluster of 2 nm.

Figure 3 shows the ^{197}Au Mössbauer spectra for the dodecanethiolate-protected Au clusters of 2 nm and 4 nm. These spectra are also fitted by the superposition of a singlet Lorentzian and two sets of doublet Lorentzians. These components correspond to those of $\text{Au}_{25}(\text{SG})_{18}$, **c1**, **c2**, and **c3**. The Mössbauer parameters (IS , QS , area) of **c1**, **c2**, and **c3** for the Au cluster of 2 nm are estimated at (0.73 mm/s, 0.0 mm/s, 39.00%), (0.88 mm/s, 3.47 mm/s, 43.70%), (2.60 mm/s, 6.90 mm/s, 17.30%), respectively. In the case of the Au cluster of 4 nm, on the other hand, those of **c1**, **c2**, and **c3** are estimated at (0.35 mm/s, 0.0 mm/s, 56.80%), (0.51 mm/s, 3.07 mm/s, 37.70%), (2.23 mm/s, 6.51 mm/s, 5.60%), respectively. In the case of dodecanethiolate-protected Au cluster of 4 nm, the Au core atoms free from dodecanethiolate are dominant.

4 Conclusion

We have investigated the structures and electronic states of a series of glutathionate-protected Au clusters, $\text{Au}_n(\text{SG})_m$ with $n = 10 - \text{Au}_{\sim 55}(\text{SG})_m$ and dodecanethiolate-protected Au clusters of 2 nm and 4 nm using ^{197}Au Mössbauer spectroscopy, which allows us to probe local environment of the constituent Au atoms via isomer shift (*IS*) and quadrupole splitting (*QS*) and area. The spectral profile of ^{197}Au Mössbauer spectrum abruptly changes on going from $\text{Au}_{22}(\text{SG})_{17}$ to $\text{Au}_{25}(\text{SG})_{18}$, then it smoothly changes to that of $\text{Au}_{\sim 55}(\text{SG})_m$. However, the profile dramatically changes on going from $\text{Au}_{\sim 55}(\text{SG})_m$ to the dodecanethiolate-protected Au cluster of 2 nm. The ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ and dodecanethiolate-protected Au clusters of 2 nm and 4 nm were successfully analyzed on the basis of the structure and electronic state of $\text{Au}_{25}(\text{SG})_{18}$.

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References

1. Clusters and Colloids; Schmid, G. (ed.) VCH: Weinheim, Germany (1994). (b) Daniel, M.-C., Astruc, D.: Chem. Rev. **104**, 293 (2004)
2. Schaff, T.G., Whetten, R.L.: J. Phys. Chem. **B104**, 2630 (2009). (b) Price, R.C., Whetten, R.L.: J. Am. Chem. Soc. **127**, 13750 (2005). (c) Tsunoyama, H., Negishi, Y., Tsukuda, T.: J. Am. Chem. Soc. **128**, 6036 (2006)
3. Negishi, Y., Nobusada, K., Tsukuda, T.: J. Am. Chem. Soc. **127**, 5261 (2005). (b) Shichibu, Y., Negishi, Y., Tsunoyama, H., Kanehara, M., Teranishi, T., Tsukuda, T.: Small **3**, 835 (2007). (c) Jin, R., Qian, H., Wu, Z., Zhu, Y., Zhu, M., Mohanty, A., Garg, N.: J. Phys. Chem. Lett. **1**, 2903 (2010). (d) Parker, J.F., Fields-Zinna, C.A., Murray, R.W.: Acc. Chem. Res. **43**, 1289 (2010)
4. Ikeda, K., Kobayashi, Y., Negishi, Y., Seto, M., Iwasa, T., Nobusada, K., Tsukuda, T., Kojima, N.: J. Am. Chem. Soc. **129**, 7230 (2007)
5. Iwasa, T., Nobusada, K.: J. Phys. Chem. C **111**, 45 (2007)
6. Heaven, M.W., Dass, A., White, P.S., Holt, K.M., Murray, R.W.: J. Am. Chem. Soc. **130**, 3754 (2008). (b) Zhu, M., Lanni, E., Garg, N., Bier, M.E., Jin, R.: J. Am. Chem. Soc. **130**, 1138 (2008)
7. Akola, J., Walter, M., Whetten, R.L., Häkkinen, H., Grönbeck, H.: J. Am. Chem. Soc. **130**, 3756 (2008)
8. Tsukuda, T., Negishi, Y., Kobayashi, Y., Kojima, N.: Chem. Lett. **40**, 1292 (2011)
9. The $\text{Au}_{55}(\text{SG})_m$ has not completely been isolated. Therefore, $\text{Au}_n(\text{SG})_m$ with the distribution of Au atoms around $n = 55$ represents $\text{Au}_{\sim 55}(\text{SG})_m$
10. Kimura, K., Sugimoto, N., Sato, S., Yao, H., Negishi, Y., Tsukuda, T. J. Phys. Chem. C **113**, 14076 (2009)
11. Nagaoka, O., Harada, G., Sugawara, T., Sasaki, A., Ito, Y.: Jpn. J. Appl. Phys. **43**, 7742 (2004)
12. MossWin 3.0 Dr. Zoltan Klencsar, <http://www.netx.hu/mosswinn/index.html>
13. Mössbauer Handbooks: ^{197}Au Mössbauer spectroscopy, Mössbauer Effect Data Center, The University of North Carolina, U.S.A. (1993)