

One-Pot Preparation of Subnanometer-Sized Gold Clusters via Reduction and Stabilization by *meso*-2,3-Dimercaptosuccinic Acid

Yuichi Negishi and Tatsuya Tsukuda*

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and Department of Photoscience, School of Advanced Sciences, The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, Japan

Received December 14, 2002; E-mail: tsukuda@ims.ac.jp

Since the pioneering work by Brust and co-workers in 1994,¹ monolayer-protected metal clusters (MPCs)² have gained much attention in various areas of science and technology. Main interests of the MPCs are focused on their optical,³ electronic,⁴ and catalytic⁵ properties which deviate significantly from those of their corresponding bulk metal. Because such a deviation becomes prominent when the core dimensions are reduced to a subnanometer range, the small MPCs will provide promising candidates for a new class of cluster-based materials. However, the reports on the subnanometer-sized MPCs are rather limited due, in part, to the fact that their preparative methods have been virtually unexplored.^{6,7} The subnanometer-sized gold MPCs have been prepared by exchanging the phosphine ligands of the Au₁₁ cluster compounds⁸ for various thiols.⁶ In a previous work, we have demonstrated that subnanometer-sized palladium MPCs are formed via the reactions between Pd^{II} salts with alkanethiol RSH molecules; RSH acts as both the reducing agents of the Pd^{II} ions and the stabilizing ligands of the resultant clusters.⁷ We report herein a one-pot preparation of the gold clusters composed of ~10–13 atoms by using a dithiol molecule, *meso*-2,3-dimercaptosuccinic acid (DMSA, **1**), as the reducing and stabilizing agents.

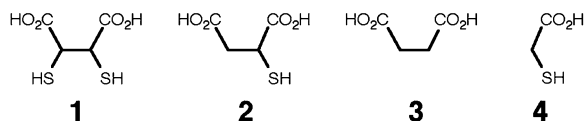


Figure 1a shows a representative TEM micrograph of the Au:DMSA clusters which are produced by mixing HAuCl₄ and DMSA with a molar ratio of 1:2 in water (see Supporting Information for more details). The mean particle diameter is 2.6 nm with a standard deviation of 0.6 nm (Figure 1b). The Au 4f_{7/2} binding energy of the Au:DMSA clusters was determined to be 84.7 eV by X-ray photoelectron spectroscopy (see Supporting Information); this value is slightly larger than that of bulk Au (83.8 eV) and similar to those of the Au:SR clusters (83.9–84.4 eV).⁹ These findings clearly illustrate that **1** can reduce the Au^{III} ions, and the gold(0) clusters result. To shed light on the origin of the reducing ability of **1**, the yields of the gold clusters were compared by using mercaptosuccinic acid (**2**) or succinic acid (**3**) instead of **1**. Qualitatively speaking, the formation of the clusters is enhanced in the order of **1** >> **2** > **3**, where no clusters are formed in the case of **3**. Thus, the SH moiety plays a crucial role in the reduction of the Au^{III} species via 2Au^{III} + 6RSH → 2Au⁰ + 3RSSR + 6H⁺. In addition, the cluster formation is greatly suppressed by using mercaptoacetic acid (**4**) instead of DMSA. The higher reducing ability of **1** as compared to that of **4** suggests that intramolecular S–S bond formation promotes the reduction. The resultant disulfides and/or unreacted DMSA may passivate the cluster surfaces through the Au–S bond formation. FT-IR spectroscopy confirms that a peak associated with the S–H

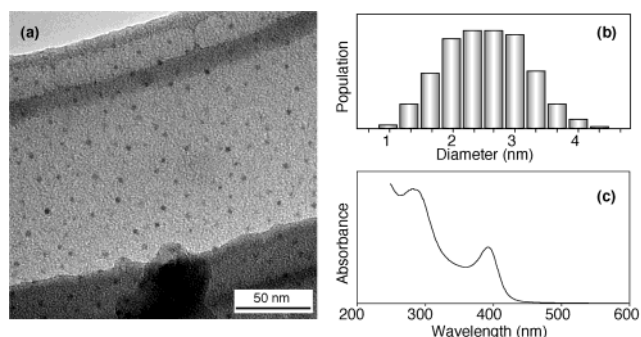


Figure 1. (a) TEM image, (b) size distribution, and (c) optical spectrum of the Au:DMSA clusters prepared by mixing HAuCl₄ and DMSA with a molar ratio of 1:2 in water (pH ~4).

stretching vibrational mode of **1** disappears when DMSA molecules are adsorbed on the Au cluster surface (Supporting Information).

The optical spectrum of the Au:DMSA clusters exhibits absorption onset at ca. 550 nm and peak structures at ca. 300 and 390 nm (Figure 1c). These features are completely different from that of the nanometer-sized gold MPCs (>2 nm), which is composed of a broad background rising continuously toward shorter wavelength and an additional band at ca. 520 nm (surface plasmon band). Figure 1c rather reminds us of the spectra of the thiolate-passivated Au₁₁ clusters, which show peaks in the range of 300–450 nm.⁶ Thus, it is likely that the Au particles in Figure 1a are the assemblages of extremely small Au:DMSA clusters formed by hydrogen bondings between the COOH groups of the DMSA ligands.¹⁰ To test this hypothesis and evaluate the core diameters of individual Au:DMSA clusters, the pH of the solution was raised to 7.2, higher than the pK_a values of DMSA (2.71 and 3.43).¹¹ In the solution of pH ~7, most of the COOH groups of the DMSA ligands are dissociated into COO⁻, leading to the disassembling of the Au:DMSA clusters due to the Coulomb repulsion. Because we found these COO⁻-modified clusters are unstable against the electron beam irradiation during the TEM observation, their surfaces were subsequently modified into hydrophobic layers via ion-pair formation with the tetraoctylammonium (TOA) cations.¹² Figure 2a shows a TEM photograph of the Au:DMSA clusters extracted into the toluene phase by the action of TOABr (BrN(*n*-C₈H₁₇)₄). The dispersibility of the clusters is dramatically improved, as is evident from the comparison with Figure 1a. It is important to note that the optical spectrum of the Au:DMSA-TOA clusters is essentially the same as that of the Au:DMSA clusters, showing the core structures are not altered by the disassembly treatment (Figure 2b). The sizes of the Au cores appear to be less than ca. 1 nm, although we cannot determine the core sizes precisely due to the poor contrast for the small particles and limited resolution of a CCD detector of the TEM apparatus.

The core size distributions of the Au:DMSA-TOA clusters were

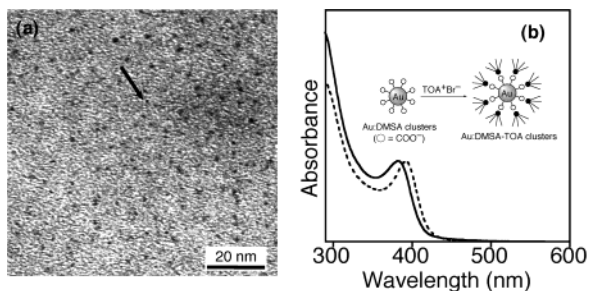


Figure 2. (a) TEM image and (b) optical spectra of the Au:DMSA-TOA clusters in toluene (solid line) and the Au:DMSA clusters dispersed in water of pH 7.2 (dotted line). The core size of the cluster indicated by the arrow in (a) is 1 nm.

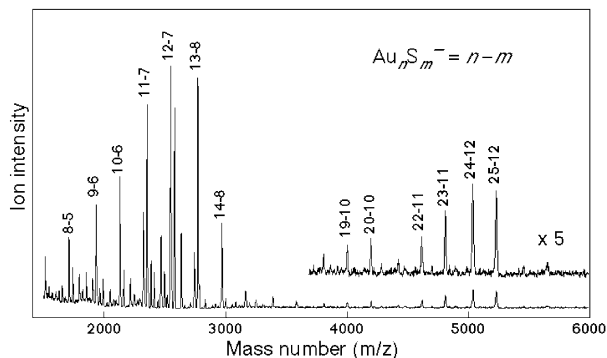


Figure 3. Negative-ion laser desorption mass spectrum of the Au:DMSA-TOA clusters. Third harmonics of a Nd:YAG laser (355 nm) was used in the ionization.

examined in detail by mass spectrometry. Figure 3 represents a negative-ion laser desorption ionization (LDI) mass spectrum. The ions formulated as $Au_nS_m^-$ are detected as a result of the UV-induced cleavage of S–C bonds of the DMSA ligands; the $Au_nS_m^-$ ions have also been observed in the LDI mass spectra of the other Au:SR clusters.¹³ The TOA molecules are released concurrently with the S–C bond breaking. Even when the laser fluence was increased up to $40 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$, we found no signs of dissociative loss of Au and/or S atom(s) but the enhancement of population of the larger clusters ($n \approx 25$) with respect to the smaller ones ($n \approx 13$); this behavior is probably due to the fact that more photons are needed to dissociate all of the S–C bonds of the larger clusters. Thus, the size distributions of the $Au_nS_m^-$ ions closely reflect those of the Au:DMSA-TOA clusters formed in the reaction. It is concluded from Figure 3 that the gold clusters composed of ~ 10 – 13 atoms are dominantly produced in the reactions, being consistent with the TEM measurements (Figure 2a). It is noticeable that the ions with the formula of $Au_{13}S_8^-$ are extraordinarily abundant in the mass spectra, suggesting the greater stability of the parents as compared to that of the neighbors. Because DMSA can possibly be adsorbed onto the cluster surface by using one or two sulfur site(s), the parents of the $Au_{13}S_8^-$ ions could be either $Au_{13}(\text{DMSA})_8$ or $Au_{13}(\text{DMSA})_4$. Elemental analysis of the Au:DMSA clusters supports the former composition; energy

dispersive spectroscopy (EDS) gives a ratio of $[\text{S}]/[\text{Au}] = 1.25$. A possible structural model for the $Au_{13}(\text{DMSA})_8$ cluster is such that eight (111) facets of the cuboctahedral Au_{13} cores are fully passivated by eight DMSA ligands. Preferential adsorption of DMSA on the (111) facet is supported by a recent theoretical study on the $Au_{13}(\text{SCH}_3)$ cluster;¹⁴ the bonding of SCH_3 to the (111) hollow site is energetically more favorable than that to the (111) bridge site and (100) hollow site.

In summary, we report herein a simple method for preparing gold MPCs by utilizing the reducing and stabilizing abilities of the DMSA molecules. Mass spectroscopic analysis reveals the core sizes of the Au:DMSA clusters are rather monodisperse and are distributed mainly in the range of 10–13 (ca. 0.8 nm). The reactions between thiols and metal salts will provide a versatile, easy, and unique method to synthesize subnanometer-sized MPCs.

Acknowledgment. We thank Prof. Hidehiro Sakurai of Osaka University and Prof. Takashi Nagata of the University of Tokyo for their valuable comments. This work was supported by a Grant-in-Aid for Creative Scientific Research Collaboratory on Electron Correlations (13NP0201) and the 2002th-year Joint Research Project (Soken/K02-1) of Sokendai.

Supporting Information Available: Experimental details, XPS data, FT-IR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
- (2) Templeton, A. C.; Wueling, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.
- (3) (a) Wilcoxon, J. P.; Martin, J. E.; Parsapour, F.; Wiedenman, B.; Kelly, D. F. *J. Chem. Phys.* **1998**, *108*, 9137. (b) Bigioni, T. P.; Whetten, R. L.; Dag, Ö. *J. Phys. Chem. B* **2000**, *104*, 6983. (c) Huang, T.; Murray, R. W. *J. Phys. Chem. B* **2001**, *105*, 12498. (d) Link, S.; Beeby, A.; FitzGerald, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2002**, *106*, 3410.
- (4) See, for example: Simon, U. *Adv. Mater.* **1998**, *10*, 1487.
- (5) (a) Zhong, C.-J.; Maye, M. M. *Adv. Mater.* **2001**, *13*, 1507. (b) Lou, Y. B.; Maye, M. M.; Han, L.; Luo, J.; Zhong, C.-J. *Chem. Commun.* **2001**, 473.
- (6) Woehrle, G. H.; Warner, M. G.; Hutchison, J. E. *J. Phys. Chem. B* **2002**, *106*, 9979.
- (7) Negishi, Y.; Murayama, H.; Tsukuda, T. *Chem. Phys. Lett.* **2002**, *366*, 561.
- (8) Jahn, W. *J. Struct. Biol.* **1999**, *127*, 106 and references therein.
- (9) (a) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17. (b) Johnson, S. R.; Evans, S. D.; Mahon, S. W.; Ulman, A. *Langmuir* **1997**, *13*, 51.
- (10) (a) Chen, S.; Kimura, K. *Langmuir* **1999**, *15*, 1075. (b) Simard, J.; Briggs, C.; Boal, A. K.; Rotello, V. M. *Chem. Commun.* **2000**, 1943. (c) Shiraishi, Y.; Arakawa, D.; Toshima, N. *Eur. Phys. J. E* **2002**, *8*, 377.
- (11) Crisponi, G.; Cristiani, F.; Nurchi, V. M.; Pinna, R.; Estévez, M. J. T. *Polyhedron* **1999**, *18*, 3257.
- (12) (a) Yao, H.; Momozawa, O.; Hamatani, T.; Kimura, K. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2675. (b) Yao, H.; Momozawa, O.; Hamatani, T.; Kimura, K. *Chem. Mater.* **2001**, *13*, 4692.
- (13) (a) Vezmar, I.; Alvarez, M. M.; Khoury, J. T.; Salisbury, B. E.; Shafiqullin, M. N.; Whetten, R. L. *Z. Phys. D* **1997**, *40*, 147. (b) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafiqullin, M.; Vezmar, I.; Whetten, R. L. *Chem. Phys. Lett.* **1997**, *266*, 91. (c) Arnold, R. J.; Reilly, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 1528.
- (14) Larsson, J. A.; Nolan, M.; Greer, J. C. *J. Phys. Chem. B* **2002**, *106*, 5931.

JA0297483