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Author(s)	Negishi, Yuichi; Arai, Rio; Niihori, Yoshiki et al.
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Isolation and structural characterization of magic silver clusters protected by 4-(*tert*-butyl)benzyl mercaptan

Yuichi Negishi,*[a] Rio Arai[a], Yoshiki Niihori[a] and Tatsuya Tsukuda[b]

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Small silver clusters (average diameter of 1.2 nm) protected by 4-(*tert*-butyl)benzyl mercaptan (BBSH) were converted to stable, monodisperse clusters (2.1 nm) by a ripening process with excess amount of BBSH. Multiple characterizations of the isolated magic clusters revealed an approximate chemical composition of $Ag_{\sim 280}(SBB)_{\sim 120}$.

Metal clusters protected by thiolates (M:SR) have attracted considerable attention as building blocks of new functional materials because they exhibit size-specific optical and physical properties. In particular, clusters with high thermodynamic and chemical stability are very promising candidates. Recent intensive studies have revealed a series of magic compositions for Au:SR clusters, such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{44}(SR)_{28}$, $Au_{68}(SR)_{34}$, $Au_{102}(SR)_{44}$, and $Au_{144/146}(SR)_{59/60}$.[1-6] These magic clusters can be synthesized selectively from the crude mixtures by utilizing their higher tolerance than the others against core etching by thiol molecules.[3b,3d,4b] The origins of the stability as well as the geometric structures of these gold clusters are now well understood.[2d,4a,4g,6-8]

Ag:SR clusters larger than ~5 nm have been also well studied because of their potential application in surface-enhanced Raman analysis, catalysis and conducting paste.[9-17] In contrast, little is known about the stable sizes for smaller clusters: reports on the chemical compositions of stable Ag:SR clusters are limited to only two examples, $Ag_7(DMSA)_4$[12] and $Ag_9(MSA)_8$[13b], wherein DMSA and MSA represent *meso* 2,3-dimercaptosuccinic acid and mercaptosuccinic acid, respectively. Primary reason for this lack of information on stable Ag:SR cluster sizes is that Ag:SR clusters are easily oxidized and are difficult to handle. In order to elucidate their stable cluster sizes, it is important to study on Ag:SR clusters that are not easily oxidized. Murray *et al*. have reported the formation of Ag clusters, assigned to $Ag_{140}(SBB)_{53}$, which show higher resistance to oxidation than other Ag:SR clusters, using 4-(*tert*-butyl)benzyl mercaptan (BBSH, Scheme S1, ESI†).[10] Motivated by this report, in the present work, we searched for magic Ag:SBB clusters by incubating in the presence of BBSH. We were able to convert the as-prepared, polydisperse Ag:SBB clusters into a single Ag:SBB cluster. Multiple characterizations of the magic clusters obtained revealed that their chemical composition is approximately $Ag_{\sim 280}(SBB)_{\sim 120}$.

Ag:SBB clusters were prepared under Ar atmosphere by the reduction of Ag(I)-SBB polymers, which were formed by the reaction between silver nitrate and BBSH. Transmission electron microscope (TEM) analysis revealed that the as-prepared Ag:SBB clusters (**1**) have silver cores with average diameters (d_{av}) of ca. 1.2 nm (Fig. S1(a), ESI†). Cluster **1** was incubated in neat BBSH at 60°C under Ar atmosphere. The structures of the products were studied as a function of the incubation time (T_{inc}) using TEM, mass spectrometry, optical spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TG), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD).[18]

Figure 1(a) shows positive-ion[19] electrospray ionization (ESI) mass spectra of Ag:SBB clusters before and after the reaction. A broad peak was observed in the mass spectrum of cluster **1** (T_{inc} = 0 h) in the mass region of ca. 10 and 15 kDa.[20] With increasing incubation time, the ion intensity in this region gradually decreased while multiple peaks appeared in the higher mass region. At T_{inc} = 3 h, clusters with a molecular weight (MW) of 43.5 kDa were formed, and clusters with MW = 51.8 kDa were additionally produced at T_{inc} = 6 h. The 51.8 kDa clusters prevailed over the 43.5 kDa clusters with longer incubation time and the latter eventually disappeared at T_{inc} = 24 h. Further increase in the cluster size was not observed, even at T_{in} = 96 h.

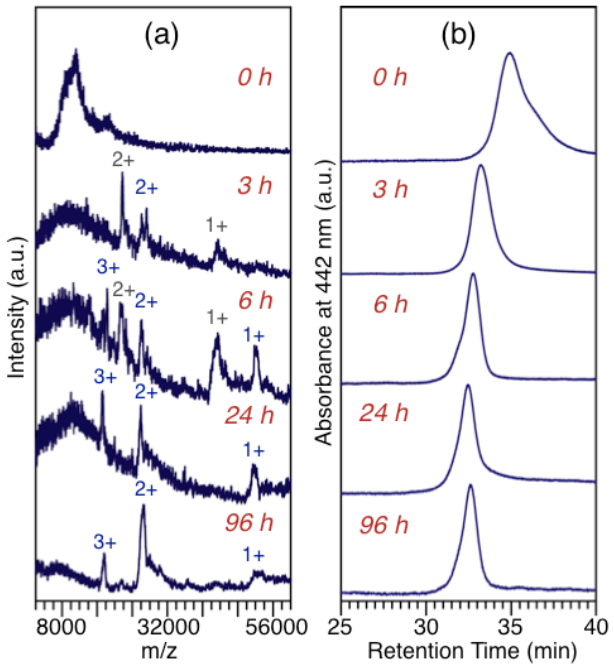

Fig. 1. (a) Positive-ion ESI mass spectra, and (b) GPC chromatograms of Ag:SBB clusters produced by the reaction of **1** with BBSH with respect to incubation time.

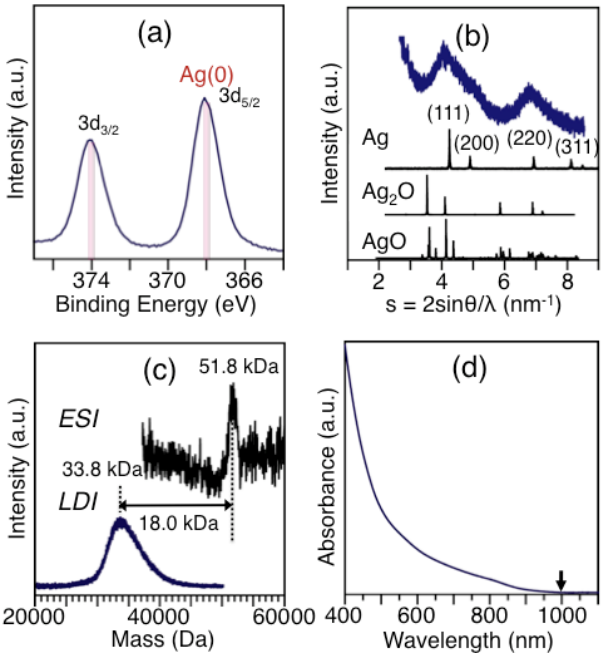

Fig. 2. (a) Ag 3d spectrum, (b) X-ray diffractogram, (c) positive-ion LDI mass spectrum, and (d) optical absorption spectrum of **2**. X-ray diffractograms of Ag, Ag_2O, and AgO are shown for comparison in panel (b). In panel (c), the top spectrum is the positive ESI mass spectrum of **2**.

These results indicate that cluster **1** was converted into 43.5 kDa clusters and finally into 51.8 kDa cluster (**2**) within 96 h at 60°C. The time required for complete conversion of **1** into **2** depended on the incubation temperature; 16 days and 6 h at 40 and 80°C, respectively (Fig. S2, ESI†).

Growth of the Ag clusters during incubation was also confirmed by GPC and TEM. Figure 1(b) shows chromatograms of the products. A broad band was observed at a retention time of 35.5 min in the chromatogram of cluster **1** (T_{inc} = 0 h). The retention time of the product gradually reduced with increasing T_{inc}. However, no further shift in the retention time was observed after 96 h, indicating that the increase in particle size was completed within T_{inc} = 96 h. TEM analysis revealed that cluster **2** has a silver core with a diameter of ca. 2.1 ± 0.2 nm (Fig. S1(b), ESI†).

Stability of cluster **2** against oxidation was studied by various methods. Figure 2(a) shows the XPS Ag 3d spectrum of cluster **2**. Broad peaks were observed in the spectrum at peak positions attributed to Ag(0) (367.9 and 373.9 eV). This indicates that the silver core of cluster **2** was not oxidized. The powder XRD pattern of cluster **2** (Fig. 2(b)) indicates the production of the Ag(0) core. The diffraction patterns of bulk Ag, Ag_2O, and AgO are also shown in the figure for comparison. Broad peaks at positions corresponding to diffractions from Ag(111), (200), (220), and (311) planes are observed for cluster **2**. In contrast, no peaks were observed at positions corresponding to AgO and Ag_2O, which indicates that the core of cluster **2** does not contain oxygen but is composed of only silver. Mass spectrometric analysis showed that cluster **2** is stable against oxidation for at least 5 days when stored in air as solid form and dispersed in toluene (Fig. S4 and S5, ESI†).

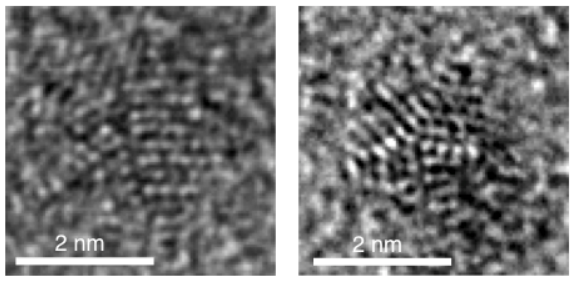

Fig. 3. HR-TEM image of **2**.

In order to determine the molecular formula of cluster **2**, we evaluate the number of BBS ligands on the silver core using laser desorption ionization (LDI) mass spectrometry. Figure 2(c) shows the positive ion LDI mass spectrum of cluster **2**. The ESI mass spectrum of cluster **2** is also shown for comparison. A broad peak is observed in the vicinity of ca. 33.8 kDa in the LDI mass spectrum. This peak position is shifted by ca. 18 kDa toward the lower mass side as compared to the parent mass peak in the ESI mass spectrum (ca. 51.8 kDa). For Au:SR clusters, it is known that the C-S bond of the protecting thiolates is selectively and completely dissociated by laser irradiation.[21-24] Since similar laser-induced dissociation was also reported for Ag:SR clusters,[13(b)(c)] this decrease in mass can be ascribed to desorption of the arylgroup of SBB due to C-S bond dissociation. A decrease in the mass of 18 kDa corresponds to dissociation of ~120 BBS aryl groups. Thus, it is considered that the chemical composition of cluster **2** can be approximated as $Ag_{280}(SBB)_{120}$. The weight ratio of Ag to BBS obtained by TG analysis (58.9%, 41.1%) was consistent with that for $Ag_{\sim280}(SBB)_{\sim120}$ (58.4%, 41.6%). On the basis of these results, we conclude that the stable cluster **2** has a chemical composition of $Ag_{\sim280}(SBB)_{\sim120}$. A similar mass spectrometric analysis of 43.5 kDa clusters revealed that they are expressed as $Ag_{\sim223}(SBB)_{\sim108}$ (Fig. S5, ESI†).

Optical absorption spectrum of cluster **2** is shown in Figure 2(d). It exhibits absorption onset at ca. 1000 nm and slight shoulders at ca. 700 and 800 nm, indicating the molecular-like electronic structure of cluster **2**. A surface plasmon band (ca. 420 nm) was not observed in contrast to $Ag:SC_{12}$ (d_{av} = 1.8 nm).[9] This discrepancy is ascribed either to the difference in thiolates used[15] or to contribution from larger $Ag:SC_{12}$ clusters contained as impurity in ref. 9.

These results reveal that as-prepared Ag:SBB clusters with d_{av} = 1.2 nm were focused into stable, monodisperse $Ag_{\sim280}(SBB)_{\sim120}$ via $Ag_{\sim223}(SBB)_{\sim108}$ by a ripening process with excess amount of BBSH.[25] It should be stressed here that size focusing via cluster growth is in sharp contrast to that by size reduction of Ag cores in digestive ripening[16b,26] and Au cores in core etching.[3b,3d,4b] There are several possible explanations for the selective production of $Ag_{\sim280}(SBB)_{\sim120}$. One possibility is that growth of the Ag core is kinetically hindered by the formation of a curved monolayer of BBS; ~120 molecules of BBS having a bulky head group may form a monolayer which fit the curvature of an Ag core. Another possibility is intrinsic stability arising from geometrical and

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electronic shell closure. In order to explore this further, we studied the geometrical structure of the Ag core of cluster **2** in more detail using high-resolution TEM. Figure 3 shows a representative HR-TEM micrograph of cluster **2**; Ag particles having 5-fold symmetry can be observed in the HR-TEM micrograph. For Au:SR clusters, it has been revealed that the stable clusters consist of the metal core having 5-fold symmetry surrounded by multiple Au(I)-thiolate oligomers.[2d,4a,4g,6-8] Figure 3 suggests that cluster **2** also has a core with a similar structure to that of stable Au:SR clusters. By assuming the density of bulk Ag (10.5 g/cm^3), we can estimate the number of the silver atoms in 2.1 nm cluster to be ~227. This is smaller than that determined by mass spectrometry and suggests the formation of Ag-thiolate oligomer interface. We must await the single crystal XRD to determine the structure.

To summarize, we have succeeded in demonstrating the size convergence of Ag:SBB clusters into a chemically stable cluster. Experiments revealed that the stable cluster has the chemical composition of $Ag_{\sim 280}(SBB)_{\sim 120}$. This cluster is size-selectively synthesized by reaction with BBSH. It is anticipated that this facilitates their crystallization and full structure determination, which is essential for understanding the origin of the stability and the exceptional physical properties of Ag:SR clusters.

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[a] *Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. Fax: +81-3-5261-4631; Tel: +81-3-5228-9145; E-mail: negishi@rs.kagu.tus.ac.jp*

[b] Catalysis Research Center, Hokkaido University, Nishi, 10, Kita 21, Sapporo 001-0021, Japan.

† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization. See DOI: 10.1039/b000000x/

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20 Although relative population between ~10 and ~15 kDa clusters changed depending on the batch, the final product obtained by incubation was always 51.8 kDa clusters.

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