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Magic Numbers of Gold Clusters Stabilized by PVP

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Transition metal clusters stabilized by polymers offer an ideal platform to study the size dependence of catalysis because rarefactional passivation by polymers allows reactants to access the cluster surface for catalysis and the cluster size can be synthetically controlled.[1,2] We previously reported that Au clusters stabilized by poly(vinylpyrrolidone) (PVP) exhibit high catalytic activity for aerobic oxidation reactions when the average diameter of the Au clusters is reduced to the 1-nm regime.[1e−g,i] One can ask whether or not a single atom is of consequence in the catalysis of Au:PVP, as is the case for bare Au clusters isolated in the gas phase or supported on a solid surface.[3] To address this question, it is indispensable to probe the cluster size with atomic resolution using mass spectrometry. A demanding task for mass analysis is that Au clusters embedded in a PVP protecting layer must be ionized and desorbed intact into the gas phase since the molecular weight and the numbers of PVP molecules interacting with Au clusters cannot be regulated experimentally in sharp contrast with the case of dendrimer-encapsulated metal clusters.[4] Using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), we have discovered a series of magic numbers for Au cluster size.

The Au clusters stabilized by PVP ($M_w = 40$ kDa) were prepared by the reduction of $AuCl_4^-$ with BH_4^- in the presence of PVP.[5] The Au:PVP clusters obtained by conventional batch mixing[1c] of the precursor and reductant solutions at 313 and 273 K are referred to as **1a** and **1b**, respectively, whereas those prepared by microfluidic mixing[1g] are named **2a** and **2b**, respectively. We first searched for the optimal conditions to probe the size distribution of the Au clusters in PVP by MALDI-MS. Our findings are summarized as follows:[5] (1) the Au cores were desorbed from the PVP layer and detected only as negative ions (Au_n^-); (2) fragmentation of the Au clusters into smaller ones during the MALDI process was suppressed considerably when the laser fluence was just above the threshold for ion detection; (3) the fragmentation of Au_n^- could be minimized by using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a matrix,[6] which has been successfully applied to the nondestructive ionization of thiolate-protected Au clusters.[7] Thus, the MALDI mass spectra of **1a**, **1b**, **2a**, and **2b** were recorded in the negative-ion mode using DCTB as the matrix under irradiation with laser light having minimum fluence (Figure 1).

The mass spectra of Au_n^- in Figure 1 indicate the size distribution of the Au cores in **1a**, **1b**, **2a**, and **2b**, since the spectral patterns are strongly dependent on the sample preparation conditions. The spectra of **1b** and **2b** indicate that the clusters produced at 273 K are smoothly distributed in the range of $n = 30-70$, regardless of the mixing methods employed. We estimate the diameter of these clusters to be 1.0−1.5 nm, which agrees well with that of Au cores determined by TEM and powder X-ray diffraction (XRD).[1i] Close inspection of the spectra of **1b** and **2b** reveals that the population of large clusters is slightly lower in **2b** than in **1b**, consistent with the results obtained using powder XRD, EXAFS, and optical spectroscopy.[1g] The mass spectra of **2a** and **1a** synthesized at a higher temperature (313 K) show the markedly pronounced mass peaks for Au_n^- at $n \approx 35$, 43, 58, 70, 110, 130, and 150. This result indicates that the synthesis of Au:PVP at the higher temperature enhances the relative population of stable clusters by depopulation of other less-stable clusters via thermal degradation. The spectra of **1a** and **2a** also show that, with an increase in the synthesis temperature, cluster growth is accelerated during batch mixing but not during microfluidic mixing; this is probably because of the rapid and homogeneous mixing in the latter. Hereafter, we refer to the cluster sizes corresponding to the local maximum intensities in the mass spectra as *magic numbers.* We determine the magic numbers to be 35 ± 1, 43 ± 1, 58 ± 1, 70 ± 3, 107 ± 4, 130 ± 1, and 150 ± 2, by statistical analysis of the mass spectra recorded under various conditions (e.g., laser fluence, [DCTB]/[Au atom] ratio) and using different samples prepared under different conditions.[5] We conclude that Au clusters with sizes of 35 ± 1, 43 ± 1, and 58 ± 1 are originally abundant in **2a**, although the asymmetric shape of the size distributions in the vicinity of these magic numbers (Figure 1, inset) suggests loss of a few Au atoms from the clusters during the MALDI process. To the best of our knowledge, this is the first observation of magic numbers for metal clusters stabilized by linear polymers such as PVP.

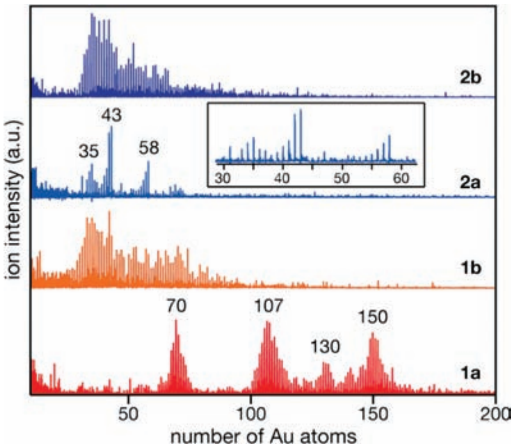

Figure 1. Representative negative-ion MALDI mass spectra of Au:PVP samples prepared by the batch reduction (**1a**, **1b**) and microfluidic synthesis (**2a**, **2b**). Inset shows a close-up of panel **2a**.

We now discuss the origin of the magic numbers in light of the electronic or geometric structure of the Au core. It is established that the magic numbers of free Au clusters are 8, 18, 20, 34, 40, 58, 92, 138,..., which is explained in terms of closure of the electronic shells created by spherical potentials. This concept was originally introduced in alkali metal clusters with the $(ns)^1$ configuration.[8] The magic numbers we observe are plotted in Figure

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10.1021/ja908188f © 2009 American Chemical Society

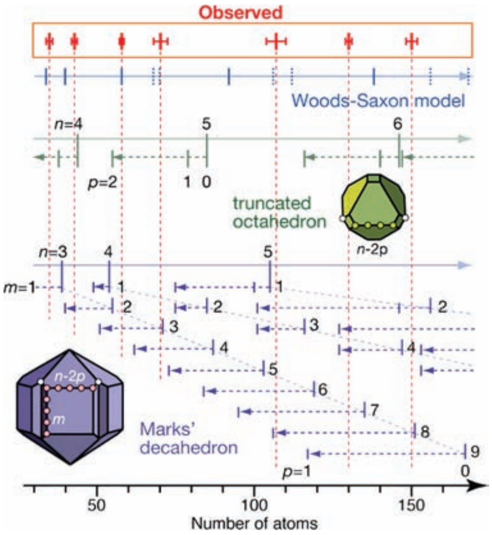

Figure 2. Magic numbers observed experimentally (red) and predicted from various models. The electronic shell model based on the Woods−Saxon potential (blue), the truncated octahedron model (green), Ino's or Marks' decahedron model (purple). The structural parameters n, m, and p are given in the inset. Dotted arrows indicate the truncation.

2 and compared with those predicted assuming the Woods−Saxon (WS) potential.[9] The magic numbers 35 ± 1, 43 ± 1, and 58 ± 1 are in reasonable agreement with those of the electronic shell model, implying that the corresponding clusters are nearly spherical in shape, which is consistent with the proposed structures for free Au^{34} and Au^{58}.[10] The slight deviation from the electronic shell model is probably caused by either the negative charge of the Au core imposed by PVP[1i] and/or deformation of the electronic potential surface of the Au core due to interaction with PVP or an asymmetric geometrical structure. The abrupt decrease in the intensity beyond these magic numbers indicates that the stability of small Au clusters is significantly affected by small differences in the electron number, i.e., even when the electron number changes by unity.

In contrast, the larger magic numbers 107 ± 4, 130 ± 1, and 150 ± 2 obviously deviate from those of the electronic shell model. To understand this, we consider the closing of the geometrical shells. Among several fcc-based nanocrystallites, cuboctahedron is the most widely proposed structural model for PVP-stabilized metal clusters.[11] Decahedral and icosahedral motifs are also candidates since they were observed in thiolate-protected clusters[12] and free Au clusters with diameters greater than 3 nm.[13] We plot in Figure 2 the cluster sizes of octahedral and decahedral motifs with various degrees of truncation. The magic numbers of an icosahedron are not shown since they are the same as those of a cuboctahedron. None of the sequences predicted for symmetrical structures can explain the observed sequence (Figure 2, red). Namely, the appearance of the magic numbers ($>\sim 107$) cannot be ascribed to an inherent stability of the Au clusters themselves. We speculate that, upon protection by PVP, the electronic and geometric structures of the Au_n cores ($n \approx 107$, 130, and 150) are substantially modified, and the cores become more stable than their neighbors.

In summary, MALDI-MS reveals a series of magic numbers in Au clusters stabilized by PVP. Magic numbers smaller than ~70 agree with those of free clusters and can be explained qualitatively by the electronic shell model. In contrast, magic numbers larger than ~100 are obviously different from those of the free clusters. We suggest that the deviation from the electronic shell model is due to perturbation of the electronic and/or geometric structures caused by interaction with PVP. Although the origin of the magic numbers remains an open question, MALDI-MS analysis can be used to synthesize size-controlled Au clusters with atomic precision.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18064017, Synergy of Elements) from MEXT and a CREST grant from JST, Japan. H.T. was financially supported by a Research Fellowship from the JSPS for Young Scientists.

Supporting Information Available: The preparation of clusters, the laser power dependence of mass spectra, and the statistical analysis of magic numbers. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA908188F