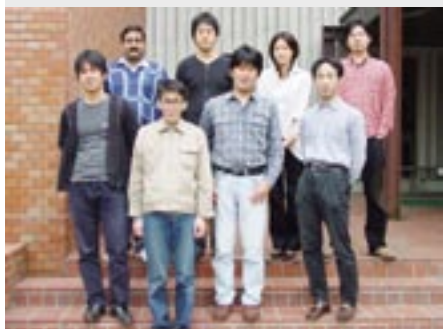


Structure and Properties of Metal Clusters Protected by Organic Molecules

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1. Extremely High Stability of Glutathionate-Protected Au₂₅ Clusters against Core Etching¹⁾

It is well known that so-called magic-numbered clusters can be preferentially populated by dissociative excitation of larger precursors, because the energy required for removal of a single atom from a magic-numbered cluster is higher than from a neighbor. Thus, if the Au atoms can be removed sequentially from preformed thiolated-protected gold (Au:SR) clusters, one can anticipate a population growth of certain stable Au_n:SR clusters. Chemical etching by free thiols is one feasible method for core size reduction of the Au:SR clusters. The etching rate of Au_n:SR clusters must be determined as a function of core size, in order to provide a synthesis for well-defined Au_n(SR)_m clusters in large quantity, as well as to provide information regarding the stability of Au_n(SR)_m. In the present paper, we studied etching reactions of Au_n(SG)_m clusters with (n,m) = (10,10), (15,13), (18,14), (22,16), (25,18), (29,20), (33,22), (39,24) by free glutathione (GSH). It was found that Au₂₅:SG clusters show higher stability against etching than the others and as a result two different reaction modes are operative depending on the core size. The Au_n(SG)_m (n < 25) clusters are completely oxidized to Au(I):SG complexes while Au_n(SG)_m (n ≥ 25) clusters are etched into Au₂₅:SG by free GSH molecules. On the basis of this observation, a model is proposed to explain our recent finding that Au₂₅(SG)₁₈ clusters are selectively formed during the reaction of triphenylphosphine-stabilized Au₁₁ clusters and an excess amount of GSH.

2. Formation of Alkanethiolate-Protected Gold Clusters with Unprecedented Core Sizes in the Thiolation of Polymer-Stabilized Gold Clusters²⁾

We have investigated magic-number sequences of octadecanethiolate-protected gold (Au:SC₁₈) clusters obtained by thiolation of gold clusters stabilized by poly(N-vinyl-2-pyr-

rolidone) (PVP). The Au:SC₁₈ clusters were prepared by the reaction of C₁₈SH and PVP-stabilized Au clusters. Four samples were fractionated by recycling size exclusion chromatography (SEC) of the as-prepared Au:SC₁₈ clusters, and their core sizes were determined to be 8, 11, 21, 26 kDa by using laser desorption ionization mass spectrometry. Unexpectedly, the sequence of these core sizes is different from that (8, 14, 22, and 29 kDa) obtained by conventional reduction of Au(I)-SC₁₈ polymers, which is governed by kinetic factors. The present finding shows that the Au:SR (R = organic group) clusters with a high tolerance to thiol etching can be systematically synthesized by first populating precursory Au clusters in a PVP matrix with subsequent thiolation of the preformed Au clusters. Optical spectroscopy shows that the electronic structure changes drastically with a core size in the size range between ca. 40 and ca. 140 atoms.

3. Thiolate-Induced Structural Reconstruction of Gold Clusters Probed by ¹⁹⁷Au Mössbauer Spectroscopy³⁾

Several research groups have recently synthesized Au:SR clusters with well-defined chemical compositions, such as Au₂₅(SR)₁₈, Au₃₈(SR)₂₄, and Au₅₅(SR)₃₂, using size-separation techniques in combination with mass spectrometry. Nevertheless, geometric structures of Au:SR have not been determined experimentally mainly due to the unavailability of single crystals of these compounds. The lack of structural information for small Au:SR clusters hinders a full understanding of the origin of their stability and novel properties (e.g. photoluminescence, magnetism, and optical activity).

In the present study, we investigated the structures of a series of glutathionate-protected gold clusters, Au_n(SG)_m with n = 10–45, using ¹⁹⁷Au Mössbauer spectroscopy, which allows us to probe the local environment of the Au sites via isomer shift (IS) and quadrupole splitting (QS). The spectral analysis, with the help of recent theoretical results on methanethiolated gold clusters, revealed that Au-SG oligomeric rings are preferentially formed around the Au core. Specifically, a core-in-

cage structural motif theoretically predicted for $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$ explains the Mössbauer spectra of $\text{Au}_{25}(\text{SG})_{18}$ fairly well and thereby explains the high stability against the core etching reaction. The positive IS and QS values for the Au cores of $\text{Au}_n(\text{SG})_m$ suggest a nontrivial effect of thiolate ligation on the electronic structure of the underlying gold clusters.

4. Synthesis of Biicosahedral Gold Clusters, $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_n\text{H}_{2n+1})_5\text{Cl}_2]^{2+}$ ($n = 2-18$)⁴

Metal clusters have been gaining growing interest as elementary units of functional materials and building blocks of optoelectronic devices because of the novelty and controllability of their properties. Probably the most interesting aspect of “cluster-assembled materials” is that new collective properties can be imparted by controlling the distance between and arrangement of individual clusters. It is not trivial, however, to achieve this goal, since the interaction between clusters has to be enhanced without causing them to coalesce. One approach that has the potential to achieve such contradictory requirements is to use “magic clusters” as building units, since the interaction between these clusters is suppressed due to their inherent stability arising from their closed electronic and geometrical structures.

This paper reports the first chemical synthesis of Au_{25} cluster compounds in which two icosahedral Au_{13} units are directly connected by sharing a single vertex atom. The chemical reaction between $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$ and n -alkanethiol $\text{C}_n\text{H}_{2n+1}\text{SH}$ ($n = 2, 8, 10, 12, 14, 16, 18$) serendipitously yielded stable Au_{25} cluster compounds with the formula, $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_n\text{H}_{2n+1})_5\text{Cl}_2]^{2+}$. Single-crystal X-ray structural analysis of $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_5)_5\text{Cl}_2](\text{SbF}_6)_2$ revealed that the Au_{25} core is constructed by bridging two icosahedral Au_{13} clusters with thiolates sharing a vertex atom (Figure 1). Optical absorption spectroscopy showed that coupling between the Au_{13} building blocks gives rise to new electronic levels in addition to those of the Au_{13} constituents.

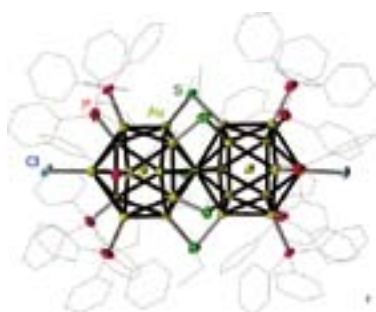


Figure 1. ORTEP drawing of the molecular structure of $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_5)_5\text{Cl}_2]^{2+}$. Thermal ellipsoids are drawn at the 50% probability level.

5. Effect of Ag-Doping on the Catalytic Activity of Polymer-Stabilized Au Clusters in Aerobic Oxidation of Alcohol⁵

We have recently showed that Au clusters ($\phi = 1.3 \pm 0.3$ nm) stabilized by a representative hydrophilic polymer, poly(*N*-vinyl-2-pyrrolidone) [PVP; $(\text{C}_6\text{H}_9\text{ON})_n$], work as catalysts for various types of aerobic oxidation in water under mild conditions.^{6,7} The Au:PVP clusters not only work as practical catalysts for aerobic oxidations, but also provide an ideal opportunity to address fundamental questions regarding the reaction mechanism. Most importantly, a wet chemical approach has enabled us to prepare monodisperse Au:PVP clusters in the core-size range of 1.3–10 nm and to study the size dependent catalytic activity. The catalytic activity per unit cluster surface was found to increase with decreasing size, which is associated with non-metallic electronic structures. With the knowledge about size effect in hand, we have launched a further investigation into the nature of the active site of the small Au:PVP by tuning the charge state of Au *via* impurity doping.

A set of nearly monodisperse Au–Ag alloy clusters (size range 1.6 to 2.2 nm) with various Ag content (5–30%) was prepared by the co-reduction method in the presence of PVP. The catalytic activities of the Au–Ag:PVP clusters were investigated for aerobic oxidation of *p*-hydroxybenzyl alcohol as a model reaction to understand the effect of Ag on the catalytic activity of Au clusters. It was found that the rate constants per unit surface area for Au–Ag:PVP clusters with small Ag content (< 10%) were larger than those of monometallic Au:PVP clusters of comparable size. The enhancement of the catalytic activity by Ag doping is discussed in light of the electronic structure of the Au–Ag cores probed by X-ray photoelectron spectroscopy. The present results indicate that the partial anionic character of the Au core is important for the aerobic oxidation reactions of Au:PVP clusters.

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Awards

NEGISHI, Yuichi; PCCP Award.

TSUKUDA, Tatsuya; GOLD 2006 Best Presentation Award.