

IX-P Structures, Stabilities and Physicochemical Properties of Organometallic Hybrid Clusters

Recently, metal clusters have gained much attention because they exhibit novel physicochemical properties that are beyond the prediction made by a dimensional scaling of those of the corresponding bulk. In this regard, metal clusters protected by thiolates or stabilized by polymers are promising candidates for elementary units of nano-scale devices. Our interests are focused on the following issues on the organometallic hybrid clusters: (1) a large-scale preparation of the subnanometer-sized clusters, (2) development of size-selection method, (3) determination of chemical compositions of size-selected clusters (*i.e.* the numbers of metal atoms and organic molecules), and (4) elucidation of effect of the core size, core shape, and interaction with organic molecules on stabilities, electronic structures, and chemical properties.

IX-P-1 Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals

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Small gold clusters (~1 nm) protected by molecules of a tripeptide, glutathione (GSH), were prepared by reductive decomposition of Au(I)-SG polymers at a low temperature and separated into a number of fractions by polyacrylamide gel electrophoresis (PAGE). Chemical compositions of the fractionated clusters determined previously by electrospray ionization (ESI) mass spectrometry¹⁾ were reassessed by taking advantage of freshly-prepared samples, higher mass resolution and more accurate mass calibration; the nine smallest components are reassigned to Au₁₀(SG)₁₀, Au₁₅(SG)₁₃, Au₁₈(SG)₁₄, Au₂₂(SG)₁₆, Au₂₂(SG)₁₇, Au₂₅(SG)₁₈, Au₂₉(SG)₂₀, Au₃₃(SG)₂₂, and Au₃₉(SG)₂₄. These assignments were further confirmed by measuring the mass spectra of the isolated Au:S(*h*-G) clusters, where *h*-GSH is a *homo*-glutathione. It is proposed that a series of the isolated Au:SG clusters corresponds to kinetically trapped intermediates of the growing Au cores. The relative abundance of the isolated clusters was correlated well with the thermodynamic stabilities against unimolecular decomposition. The electronic structures of the isolated Au:SG clusters were probed by X-ray photoelectron spectroscopy (XPS) and optical spectroscopy. The Au(4f) XPS spectra illustrate substantial electron donation from the gold cores to the GS ligands in the Au:SG clusters. The optical absorption and photoluminescence spectra indicate that the electronic structures of the Au:SG clusters are well quantized: embryos of the sp band of the bulk gold evolve remarkably depending on the numbers of the gold atoms and GS ligands. The comparison of these spectral data with those of sodium Au(I) thiomalate and 1.8-nm Au:SG nanocrystals (NCs) reveals that the subnanometer-sized Au clusters thiolated constitute a distinct class of binary system which lies between the Au(I)-thiolate complexes and thiolate-protected Au NCs.

Reference

1) Y. Negishi *et al.*, *J. Am. Chem. Soc.* **126**, 6518 (2004).

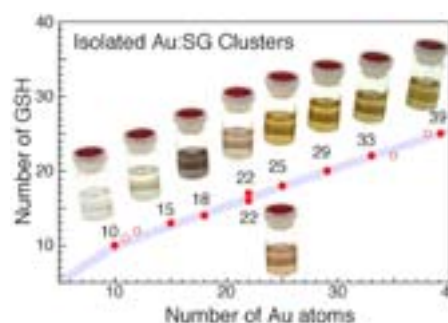


Figure 1. Chemical compositions of the Au:SG clusters isolated in the present study.

IX-P-2 Large-Scale Synthesis of Thiolated Au₂₅ Clusters via Ligand Exchange Reactions of Phosphine-Stabilized Au₁₁ Clusters

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Phosphine-stabilized Au₁₁ clusters in chloroform were reacted with glutathione (GSH) in water under a nitrogen atmosphere. The resulting Au:SG clusters exhibit an optical absorption spectrum similar to that of Au₂₅(SG)₁₈, which was isolated as the major product from chemically prepared Au:SG clusters.¹⁾ Rigorous characterization by optical spectroscopy, electrospray ionization mass spectrometry, and polyacrylamide gel electrophoresis confirms that the Au₂₅(SG)₁₈ clusters were selectively obtained on the sub-100-mg scale by ligand exchange reaction under aerobic conditions. The ligand exchange strategy offers a practical and convenient method of synthesizing thiolated Au₂₅ clusters on a large scale.

Reference

1) Y. Negishi *et al.*, *J. Am. Chem. Soc.* **127**, 5261 (2005).



Figure 1. Large-scale synthesis of the Au₂₅(SG)₁₈ clusters via ligand exchange reactions.

IX-P-3 Subnanometer-Sized Gold Clusters with Dual Molecular Receptors: Synthesis and Assembly in One-Dimensional Arrangements

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[*Chem. Lett.* **34**, 1638–1639 (2005)]

The gold (Au:S- β -CD) clusters modified by thiolated β -cyclodextrin (HS- β -CD) were prepared by reduction of AuCl₄⁻ with NaBH₄ in DMSO solution: the concentration ratio, [HS- β -CD]/[AuCl₄⁻], was fixed at 1. Interestingly, the core size distribution of the Au:S- β -CD clusters determined by TEM measurements exhibits bimodal core-size distribution centered at *ca.* 1.1 and 2.4 nm. These two components were successfully separated by using polyacrylamide gel electrophoresis (PAGE). The low-mobility clusters contain the Au cores with the average diameter of 2.3 \pm 0.4 nm whose optical absorption spectrum exhibits the surface plasmon band peaked at *ca.* 520 nm. In contrast, the Au clusters with the sizes of \sim 1 nm are barely discernible in the TEM image of the high-mobility clusters (**Au-1**). The optical spectroscopy and the thermogravimetric measurement suggest that fraction **Au-1** is composed of the Au_{12–15} cores protected by two β -CD ligands. Since the diameter of the circle made by seven sulfurs of the S- β -CD is comparable to the Au core size, this result inevitably implies that two S- β -CD ligands are attached to the Au core so that the hydrophobic cavities are pointed toward the opposite side. This structural hypothesis was confirmed by the formation of one-dimensional assemblies of **Au-1** through binding interaction with ferrocene dimers (see structure in Figure 1). By use of tailor-made molecules as linkers, the **Au-1** clusters may be assembled in well-ordered arrangements with desired symmetry and interparticle distance.

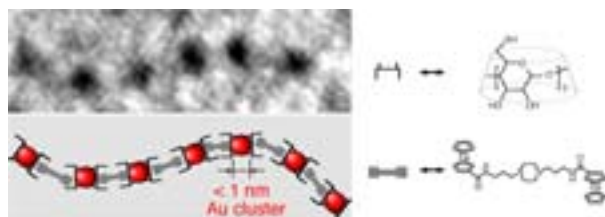


Figure 1. One-dimensional arrangements of **Au-1** formed by host-guest interaction with ferrocene dimers.

IX-P-4 Size-Specific Catalytic Activity of Polymer-Stabilized Gold Nanoclusters for Aerobic Alcohol Oxidation in Water

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Gold nanoclusters (ϕ = 1.3 nm) stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP NCs) readily oxidize benzylic alcohols to the corresponding aldehydes and/or

carboxylic acids under ambient temperature in water. Kinetic measurement revealed that smaller Au:PVP NCs exhibit higher catalytic activity than larger (9.5 nm) homologues and, more surprisingly, than Pd:PVP NCs of comparable size (1.5 and 2.2 nm). On the basis of the marked difference in the kinetic isotope effect and activation energy between Au:PVP and Pd:PVP NCs, a reaction mechanism for alcohol oxidation catalyzed by Au:PVP NCs is proposed in which a superoxo-like molecular oxygen species adsorbed on the surface of the small Au NCs abstracts a hydrogen atom from the alkoxide.

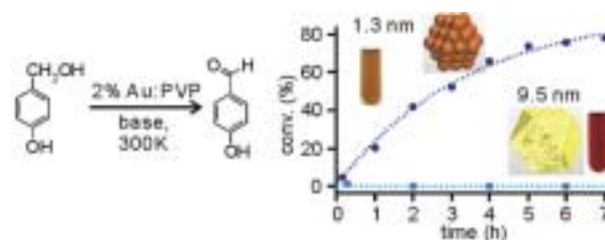


Figure 1. Time-course of conversion of *p*-hydroxyl benzyl alcohol by Au:PVP NCs (ϕ = 1.3 and 9.5 nm).

IX-P-5 Fabrication of Two dimensional Arrays of Size-Selected Gold Clusters

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Alkanethiolate-protected gold (Au:SR) clusters of the size range of 1 ~ 5 nm were prepared by a ligand exchange of polymer-stabilized gold clusters (Au:PVP)¹ dispersed in water and subsequent heat treatment.² The Au:SR clusters thus obtained were size selected by using gel permeation chromatography (GPC).³ The mass spectrometric characterization of the fractionated samples has revealed that the magic-numbered gold clusters with core masses of 8 kDa (1.1 nm), 14 kDa (1.3 nm), 22 kDa (1.5 nm), and 28 kDa (1.7 nm)⁴ can be isolated by the GPC in a recycled operation. As for the Au:SR clusters of > 2 nm, the GPC separation yielded the sized selected clusters with a resolution of one atomic shell (0.5 nm in diameter). Two-dimensional arrays of the size-selected Au:SR clusters were fabricated by Langmuir-Brodgett technique. The structures of the films transferred to the amorphous carbon and other substrates (graphite and titania) were characterized by TEM, AFM, and SEM. Fabrication of model catalytic systems by using the cluster film thus prepared is now underway in collaboration with the groups of Profs. Al-Shamery (Oldenburg Univ.) and Matsumoto (IMS).

References

- 1) H. Tsunoyama *et al.*, *Langmuir* **20**, 11293 (2004).
- 2) T. Shimizu *et al.*, *J. Phys. Chem. B* **107**, 2719 (2003).
- 3) H. Murayama *et al.*, *J. Phys. Chem. B* **108**, 3496 (2004).
- 4) T. G. Schaaff *et al.*, *J. Phys. Chem. B* **101**, 7885 (1997).