

IX-N 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-N-1 Aerobic Oxidation Catalyzed by Gold Nanoclusters as *quasi*-Homogeneous Catalysts: Generation of Hydrogen Peroxide Using Ammonium Formate

SAKURAI, Hidehiro; TSUNOYAMA, Hironori; TSUKUDA, Tatsuya

[*Trans. Mater. Res. Soc. Jpn.* **31**, 521–524 (2006)]

Gold(0) nanocluster with $d_{av} = 1.3 \pm 0.3$ nm stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP-1) showed high catalytic activity toward the generation of hydrogen peroxide in water under ambient conditions using ammonium formate as a reductant. Generation of hydrogen peroxide was monitored by tracking the conversion of *o*-tolylboronic acid to *o*-cresol. In the presence of excess ammonium formate, *o*-cresol was obtained from *o*-tolylboronic acid with ~60% yield within 24 hours at 300 K. In order to investigate the dependence of the reactivity on cluster size, monodisperse gold nanoclusters (Au:PVP-*n*; *n* = 2–4) with average diameters up to ~5 nm were prepared by the seed-mediated growth method using Na₂SO₃ as a reductant. Smaller cluster showed superior catalytic activity compared to larger clusters, suggesting that molecular oxygen species preferentially adsorbed on small Au clusters played an essential role in the formation of hydrogen peroxide.

IX-N-2 Spectroscopic Investigation of Dendrimer-Encapsulated Gold Clusters

IMAMURA, Masaki¹; MIYASHITA, Takeho¹; TANAKA, Akinori¹; YASUDA, Hidehiro¹; YANAGIMOTO, Yasushi; NEGISHI, Yuichi; TSUKUDA, Tatsuya
(¹Kobe Univ.)

[*Trans. Mater. Res. Soc. Jpn.* **31**, 517–520 (2006)]

We have carried out the spectroscopic studies of dendrimer-encapsulated Au nanoclusters smaller than 2.4 nm. In this study, a 1.5th generation sodium carboxylate-terminated polyamidamine dendrimer was used as a template to control the size and stability of Au nanoclusters. The dendrimer-encapsulated Au nanoclusters were prepared by the chemical reduction of Au ions loaded within the dendrimer templates. The synthesized smallest nanocluster used in this work shows the

strong blue photoluminescence at 2.8 eV photon energy, while larger nanocluster shows no photoluminescence. Furthermore, we carried out the X-ray photoemission study in the valence-band region of dendrimer-encapsulated Au nanocluster. From these results, we will discuss the size dependent properties of Au nanoclusters encapsulated within the dendrimer templates.

IX-N-3 Chromatographic Isolation of “Missing” Au₅₅ Clusters Protected by Alkanethiolates

TSUNOYAMA, Hironori; NEGISHI, Yuichi; TSUKUDA, Tatsuya

[*J. Am. Chem. Soc.* **128**, 6035–6037 (2006)]

We report on the first synthesis of alkanethiolate-protected Au₅₅ (11 kDa), which has been a “missing” counterpart of Schmid’s Au₅₅(PR₃)₁₂Cl₆. Au:SC_x clusters (*x* = 12, 18) were prepared by the reaction of alkanethiol (C_xSH) with polymer-stabilized Au clusters (~1.3 nm) and subsequently incubated in neat C_xSH. The resulting clusters were successfully fractionated by recycling gel permeation chromatography into Au_{~38}:SC_x and Au_{~55}:SC_x, and identified by laser-desorption ionization mass spectrometry. The Au_{~55}:SC_x clusters exhibited structured optical spectra, suggesting molecular-like properties. The thiolate monolayers were found to be liquid-like on the basis of the IR spectrum and the monolayer thickness estimated from the hydrodynamic diameter.

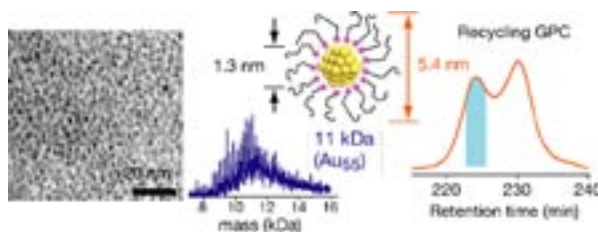


Figure 1. Isolation and characterization of Au₅₅:SC_x. [Reprinted with permission from *J. Am. Chem. Soc.* **128**, 6035–6037 (2006). Copyright (2006) American Chemical Society.]

IX-N-4 Chiroptical Activity of BINAP-Stabilized Undecagold Clusters

YANAGIMOTO, Yasushi; NEGISHI, Yuichi;

FUJIHARA, Hisashi¹; TSUKUDA, Tatsuya
(¹Kinki Univ.)

[*J. Phys. Chem. B* **110**, 11611–11614 (2006)]

Undecagold cluster compounds $[\text{Au}_{11}(\text{BINAP})_4\text{X}_2]^+$ ($\text{X} = \text{Cl}$ and Br) were synthesized by chemical reduction of the corresponding precursor complexes, Au_2X_2 (BINAP), where BINAP represents the bidentate phosphine ligand 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. The circular dichroism spectra of Au_{11} stabilized by the enantiomers $\text{Au}_{11}(\text{R-BINAP})_4\text{X}_3$ and $\text{Au}_{11}(\text{S-BINAP})_4\text{X}_3$ exhibited intense and mirror-image Cotton effect, whereas those of Au_{11}^{3+} clusters stabilized by achiral monodentate phosphine ligands did not. The origin of the chiroptical activity of $[\text{Au}_{11}(\text{BINAP})_4\text{X}_2]^+$ is discussed in the context of the structural deformation of the Au_{11}^{3+} core.

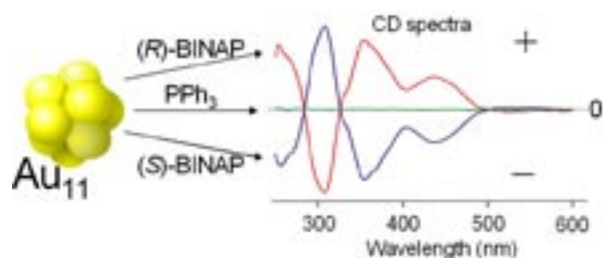


Figure 1. CD spectra of $[\text{Au}_{11}(\text{BINAP})_4\text{X}_2]^+$. [Reprinted with permission from *J. Phys. Chem. B* **110**, 11611–11614 (2006). Copyright (2006) American Chemical Society.]

IX-N-5 Kinetic Stabilization of Growing Gold Clusters by Passivation with Thiolates

NEGISHI, Yuichi; TAKASUGI, Yoshimitsu¹; SATO, Seiichi¹; YAO, Hiroshi¹; KIMURA, Keisaku¹; TSUKUDA, Tatsuya
(¹Univ. Hyogo)

[*J. Phys. Chem. B* **110**, 12218–12221 (2006)]

Small gold clusters (<1 nm), protected by monolayers of glutathione, *N*-(2-mercaptopropionyl)glycine or mercaptosuccinic acid, were prepared by reducing the corresponding Au(I)-thiolate polymers, and were fractionated by size using polyacrylamide gel electrophoresis (PAGE). Mass analysis of the fractionated clusters revealed that their core sizes varied with the molecular structures of the thiolates. This finding indicates that the reduction of the Au(I)-thiolate polymers yields small clusters whose growth is kinetically hindered by passivation with thiolates. Optical spectra of the clusters with identical compositions exhibited different profiles depending on the thiolate molecular structures, implying that deformation of the underlying gold cores is induced by inter-ligand interactions.

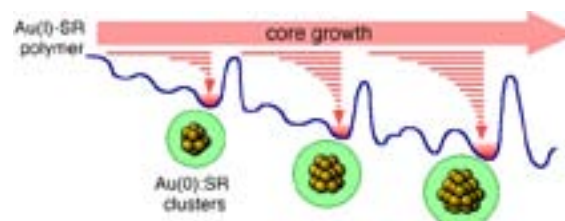


Figure 1. Kinetic stabilization of growing gold clusters by passivation with thiolates. [Reprinted with permission from *J. Phys. Chem. B* **110**, 12218–12221 (2006). Copyright (2006) American Chemical Society.]

IX-N-6 Size Effect on the Catalysis of Gold Clusters Dispersed in Water for Aerobic Oxidation of Alcohol

TSUNOYAMA, Hironori; SAKURAI, Hidehiro; TSUKUDA, Tatsuya

[*Chem. Phys. Lett.* **429**, 528–532 (2006)]

We prepared a set of nearly monodisperse gold clusters ranging from 1.3 to 10 nm by a seed-mediated growth in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP). The seed clusters with a diameter of 1.3 ± 0.3 nm were prepared by reducing AuCl_4^- with NaBH_4 in a low-temperature aqueous solution of PVP. Subsequent reduction of more AuCl_4^- by Na_2SO_3 in the presence of the seed clusters yielded a series of larger Au:PVP clusters. Catalytic activities of the Au:PVP clusters for aerobic oxidation of *p*-hydroxybenzyl alcohol increased with decrease in the core size. The size dependence is discussed in light of the electronic structures of the cores probed by optical spectroscopy.

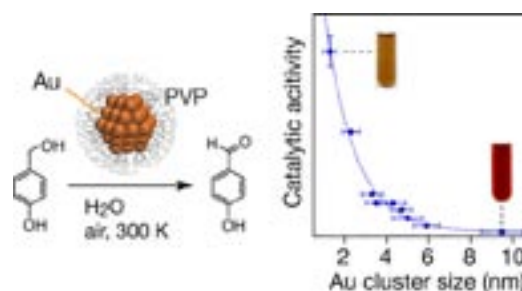


Figure 1. Catalytic activities of the Au:PVP clusters for aerobic oxidation of *p*-hydroxybenzyl alcohol increased with decrease in the core size. [Reprinted with permission from *Chem. Phys. Lett.* **429**, 528–532 (2006). Copyright (2006) Elsevier.]

IX-N-7 X-Ray Magnetic Circular Dichroism of Size-Selected, Thiolated Gold Clusters

NEGISHI, Yuichi; TSUNOYAMA, Hironori; SUZUKI, Motohiro¹; KAWAMURA, Naomi¹; MATSUSHITA, M. Michio²; MARUYAMA, Koichi; SUGAWARA, Tadashi²; YOKOYAMA, Toshihiko; TSUKUDA, Tatsuya
(¹JASRI/SPring-8; ²Univ. Tokyo)

[*J. Am. Chem. Soc.* **128**, 12034–12035 (2006)]

We report herein the X-ray magnetic circular dichroism (XMCD) at the Au $L_{2,3}$ edges of a series of Au clusters protected by glutathione (GSH). The samples used here included $Au_N(SG)_M$ with $(N, M) = (10, 10), (15, 13), (18, 14), (22, 16), (25, 18), (29, 20), (39, 24)$ and a sodium gold(I) thiomalate (SGT) as a reference. Magnetic moments per cluster were found to be increased with size, whereas those per Au–S bond were nearly constant. This finding suggests that a localized hole created by Au–S bonding at the gold/glutathione interface, rather than the quantum size effect, is responsible for the spin polarization of gold clusters.

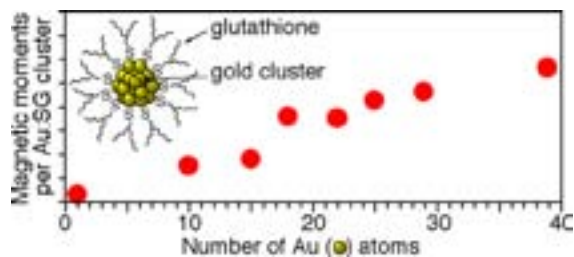


Figure 1. Magnetic moments per cluster as a function of core size.

[Reprinted with permission from *J. Am. Chem. Soc.* **128**, 12034–12035 (2006). Copyright (2006) American Chemical Society.]

IX-N-8 Mechanism of Selective Formation of Thiolated Au_{25} Clusters in Ligand Exchange of Phosphine-Stabilized Gold Clusters: Size Focusing *via* Core Etching

SHICHIBU, Yukatsu; NEGISHI, Yuichi;
TSUNOYAMA, Hironori; KANEHARA, Masayuki¹;
TERANISHI, Toshiharu¹; TSUKUDA, Tatsuya
(¹Univ. Tsukuba)

Recently, we have succeeded in large-scale selective synthesis of $Au_{25}:SG$ clusters *via* ligand exchange reactions of triphenylphosphine-stabilized Au_{11} clusters with glutathione (GSH) under optimized conditions (Shichibu, Y. *et al.* *J. Am. Chem. Soc.* **127**, 13464 (2005)). The mechanism of the selective formation of $Au_{25}:SG$ was studied by monitoring the size distribution of the ligand exchange products using electrophoresis and optical absorption spectroscopy. It was found that the core size distributions of the $Au_n:SG$ clusters extracted at the initial stage are polydisperse and are subsequently focused into $Au_{25}:SG$ in the presence of free GSH molecules. The reaction of a series of the size-selected $Au_n:SG$ clusters ($n = 10, 15, 18, 22, 25, 29, 33, 39$) with free GSH under aerobic conditions revealed that two different reaction modes are operative depending on the core size. The $Au_n:SG$ ($n < 25$) clusters are completely oxidized to $Au(I):SG$ complexes while $Au_n:SG$ ($n \geq 25$) clusters are etched into $Au_{25}:SG$ by free GSH molecules. This indicates that the “ligand exchange reaction” we referred to in our previous paper, consists of two processes, *i.e.*, a ligand exchange accompanying rapid agglomeration of Au cores and subsequent etching of the cores. We conclude that the extremely high stability of $Au_{25}:SG$ clusters against etching is the main cause for the selective formation.

Other gold clusters stabilized by polymer ($\phi = 1.3 \pm 0.3$ nm) or triphenylphosphine ($\phi = 1.5 \pm 0.4$ nm) were also converted selectively to $Au_{25}:SG$ by treatment with excess GSH, supporting the proposed mechanism.

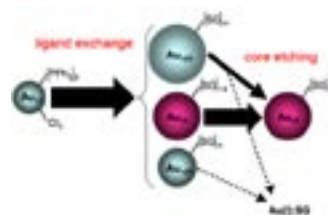


Figure 1. Mechanism of size focusing in the ligand exchange.