

VIII-J Electronic Properties of Monolayer-Protected Metal Clusters

Monolayer-protected metal clusters or nanoparticles have received much attention recently because their electronic and optical properties can be tuned by their sizes and shapes. The novel electronic properties of the clusters as well as their tunability are important from the viewpoint of future application as optoelectronic nanodevices. Our interests are focused on the following topics on the thiol-derivatized metal clusters and nanoparticles: (1) preparation and characterization of small clusters with core diameters of ~ 1 nm range (~ 40 atoms/cluster) which may exhibit molecular-like electronic and charging properties, (2) determination of structural dimensions (core diameters and monolayer thickness) of metal nanoparticles, and (3) development of size-selection method for the clusters and nanoparticles. Our goal is to reveal the evolution of electronic structures of the metal clusters as a function of the cluster size.

VIII-J-1 Development of Mass Spectrometer for Clusters

NEGISHI, Yuichi; TSUKUDA, Tatsuya

Mass spectrometry provides detailed informations on the chemical compositions of the metal clusters. We have constructed a time-of-flight (TOF) mass spectrometer which accommodates three types of ion sources: (1) a matrix-associated laser desorption/ionization (MALDI) source for clusters obtained as solid, (2) an electrospray ionization source for clusters dispersed in aqueous phase, and (3) an electron-impact ionization source for molecular clusters. Only a brief description on the MALDI/TOF apparatus, which has been developed recently, is presented here. The specimens for mass analysis are prepared by depositing an aliquot (~ 1 – 5 μ L) of the mix solutions of cluster samples and matrix onto a surface of a target made of stainless steel. After the solvent is evaporated at ambient atmosphere, the target is fed into the mass spectrometer through a load-lock chamber and attached to one of acceleration grids. The sample is irradiated with the third harmonic (355 nm) of a Nd:YAG laser operated at 10 Hz. The laser fluence is adjusted typically in the range of 10–40 μ J/mm²/pulse. The cluster ions thus formed are accelerated by applying a pulsed high voltage (15–20 kV) to the electrode plates. The ion beams are focused and stirred by ion optics and then detected by a MCP detector located at the end of the flight path of 1.17 m. Mass spectra of the ions of either polarity can be recorded by simply changing the polarities of the power supplies.

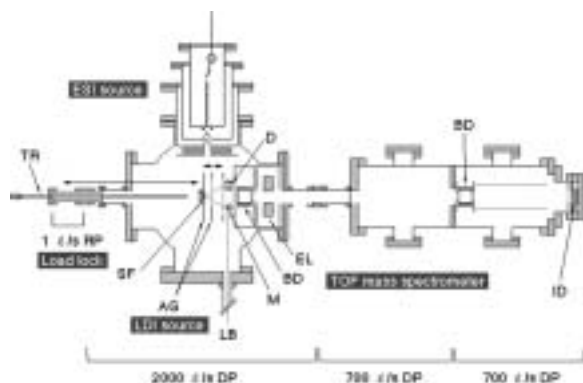


Figure 1. Schematic diagram of the apparatus: TR: transfer rod, SF: sample folder, AG: acceleration grid, LB: laser beam, M: mirror, D: damper, BD, beam deflector, EL: einzel lens, ID: ion detector. Details of the ESI source are not described here. The EI source installed perpendicularly to the diagram is not shown.

VIII-J-2 Formation of $\text{Pd}_n(\text{SR})_m$ Clusters ($n < 60$) in the Reactions of PdCl_2 and RSH ($\text{R} = n\text{-C}_{18}\text{H}_{37}$, $n\text{-C}_{12}\text{H}_{25}$)

NEGISHI, Yuichi; MURAYAMA, Haruno; TSUKUDA, Tatsuya

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Mass spectroscopic analysis revealed that Pd clusters passivated by thiolates as well as the stoichiometric thiolate complexes $\text{Pd}_n(\text{SR})_{2n}$ ($n = 5, 6$) are formed in the reactions between palladium chloride and n -alkane-thiols (RSH : $\text{R} = n\text{-C}_{18}\text{H}_{37}$, $n\text{-C}_{12}\text{H}_{25}$) in toluene. The Pd clusters thus formed are formulated as $\text{Pd}_n(\text{SR})_m$ with $m \sim 0.6n$ and the cluster size are distributed in the range of $5 \leq n \leq 60$, being consistent with core diameters of ~ 1 nm determined by TEM observations. A gap of ~ 2 eV was observed in the optical transition of the $\text{Pd}_n(\text{SR})_m$ clusters showing the emergence of non-metallic properties as a result of the size reduction.

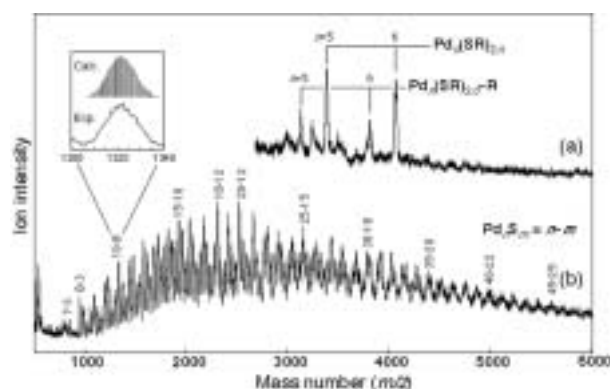


Figure 1. Typical representations of MALDI mass spectra of the mixtures of $\text{PdCl}_2/n\text{-C}_{18}\text{H}_{37}\text{SH}$ which are diluted with anthracene to (a) ~ 1 and (b) ~ 20 mol%.

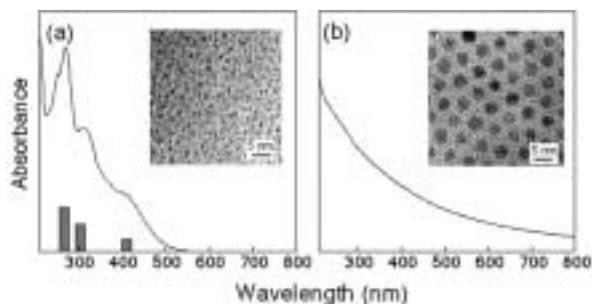


Figure 2. Optical spectra of hexane solutions of (a) $\text{PdCl}_2/n\text{-C}_{18}\text{H}_{37}\text{SH}$ mixture and (b) $\text{Pd}:\text{SC}_{18}\text{H}_{37}$ nanoparticles. The solid bars in panel (a) represent the absorbance of the $\text{Pd}_n(\text{SC}_{18}\text{H}_{37})_{2n}$ complexes ($n = 5$ and 6).

VIII-J-3 Size-Selective Preparation of Water-Soluble Gold Clusters

NEGISHI, Yuichi; TSUKUDA, Tatsuya

Colloidal solution of gold clusters was formed upon mixing AuCl or AuCl_4^- and *meso*-dimercaptosuccinic acid (DMSA: $\text{HO}_2\text{CCH}(\text{SH})\text{CH}(\text{SH})\text{CO}_2\text{H}$) in water. The size distributions of the gold clusters can be controlled by simply changing the mixing ratios of the gold salts and DMSA as revealed by optical spectroscopy and TEM observations. Figure 1 shows the uv-vis spectra of the colloidal solutions prepared with different mixing ratios between AuCl and DMSA. With increase in the ratios of DMSA, the surface plasmon band at ~ 530 nm disappears and the onset of the optical transition shifts toward shorter wavelength, implying the reduction of the cluster sizes. The TEM measurements confirm this trend: the average sizes of the Au cores are 3.1 ± 0.7 and 1.8 ± 0.6 for the mixing ratios $[\text{DMSA}]/[\text{AuCl}]$ of 1 and 2, respectively (Figure 2). These findings indicate the DMSA molecules act both as reducing agents against the $\text{Au}(\text{I})$ or $\text{Au}(\text{III})$ ions and stabilizing ligands for the resulting $\text{Au}(0)$ clusters. Optimization of preparation conditions as well as purification of the clusters by polyacrylamide gel electrophoresis (PAGE) and gel permeation chromatography (GPC) is now under way in our laboratory.

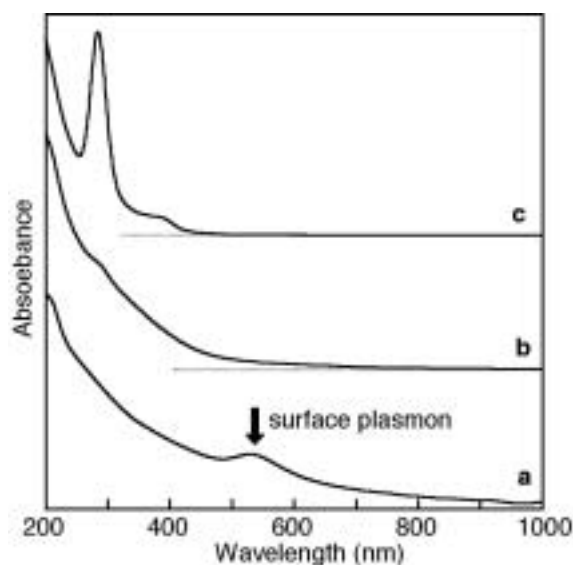


Figure 1. Optical spectra of colloidal solutions of gold clusters prepared with the mixing ratios $[\text{DMSA}]/[\text{AuCl}]$ of (a) 0.1, (b) 0.2, and (c) 0.4.

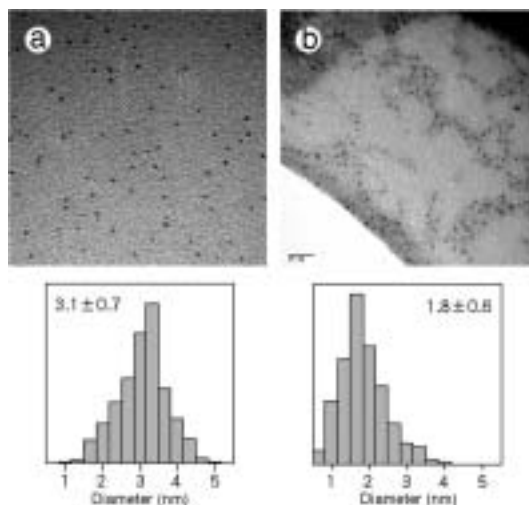


Figure 2. TEM images and size distributions of gold clusters obtained with the mixing ratios $[\text{DMSA}]/[\text{AuCl}]$ of (a) 1 and (b) 2.

VIII-J-4 Characterization and Purification of Pd:SR Nanoparticles by Gel Permeation Chromatography

MURAYAMA, Haruno; TSUKUDA, Tatsuya

Gel permeation chromatography (GPC) and transmission electron microscopy (TEM) have been used to characterize the structures of $\text{Pd}:\text{SR}$ ($\text{R} = n\text{-C}_{18}\text{H}_{37}$, $\text{C}_{16}\text{H}_{33}$, $\text{C}_{14}\text{H}_{29}$, $\text{C}_{12}\text{H}_{25}$, $\text{C}_{10}\text{H}_{21}$, C_6H_{13}) nanoparticles. The $\text{Pd}:\text{SR}$ nanoparticles are prepared by ligand exchange of PVP-protected Pd nanoparticles.¹⁾ The difference between the average diameter (D_c) measured by TEM and hydrodynamic diameter (D_h) determined by GPC allows us to determine the thickness (T) of the monolayer of alkanethiolates. On the basis of these results together with the length of free alkanethiols, a structural model of the monolayers on the Pd clusters has been proposed. It is also demonstrated that the $\text{Pd}:\text{SR}$ clusters which are size selected by GPC show pronounced tendency to self-assemble into two-dimensional superlattices (Figure 1). Further purification of the clusters by the GPC in a recycled mode is now in progress in our group.

Reference

- 1) T. Tsukuda, N. Kimura, T. Sasaki and T. Nagata, *Trans. Matr. Res. Soc. Jpn.* **25**, 929 (2000).

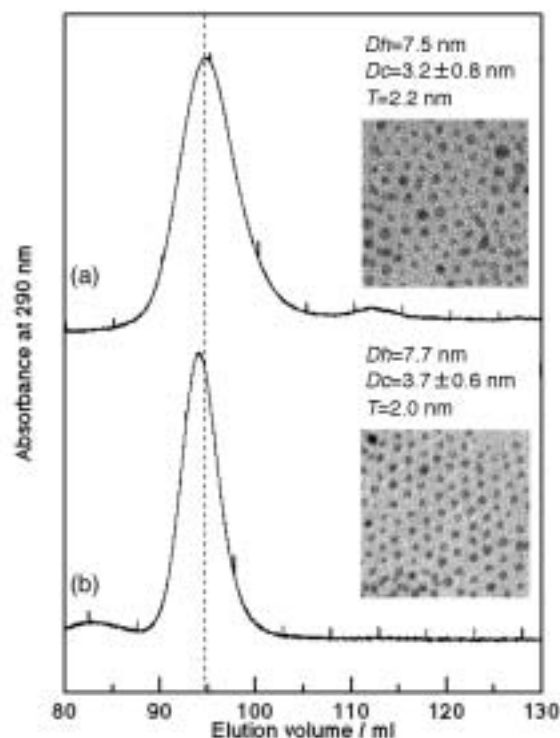


Figure 1. Chromatograms and TEM images for (a) as-prepared and (b) purified Pd:SR nanoparticles.

VIII-K Structures and Dynamics of Molecular Cluster Ions

Molecular clusters, intermediate states of matter between bulk and a molecule, provide us unique opportunities to study how the chemical and physical properties evolve with a degree of aggregation. We studied photo-induced reactions within size-selected cluster anions and evolutions of crystal structures of clusters.

VIII-K-1 Structural Evolution of Large $(\text{CO}_2)_n^-$ Clusters as Studied by Mass Spectrometry

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[*Chem. Phys. Lett.* **364**, 127 (2002)]

The mass distributions of $(\text{CO}_2)_n^-$ produced by electron-impact ionization of a free jet have been measured up to $n \sim 10^3$. Several intensity anomalies observed in a small size range are ascribed to the stabilities of the negative ions. In contrast, a series of humps are clearly discernible in the range of $n \geq 100$, which reflects the abundance of neutral $(\text{CO}_2)_n$. The intensity oscillations are analyzed in the context of “geometrical shell closings.” The analysis reveals that the $(\text{CO}_2)_n$ clusters with $n > \sim 80$ have truncated forms of an *fcc* crystal, most likely a cuboctahedral motif (Figure 1).

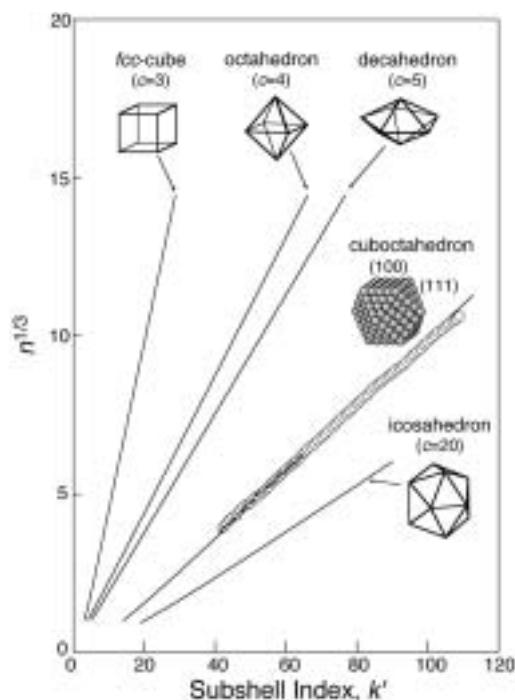


Figure 1. Plots of $n^{1/3}$ against the subshell index k' for various polyhedra. Symbols $\bigcirc$ and $\bullet$ represent the experimental data for $(\text{CO}_2)_n^-$ and $(\text{CO}_2)_n^+$, respectively. Both plots are explicable in terms of cuboctahedra (CO). The spheres in the CO motif represent the CO_2 constituent molecules.

VIII-K-2 Photochemistry of $(\text{NO})_n^-$ as Studied by Photofragment Mass Spectrometry

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[*Int. J. Mass Specrom.* **220**, 137 (2002)]

Photofragmentation of $(\text{NO})_n^-$ ($3 \leq n \leq 21$) in the energy range 2.7–3.6 eV (350–460 nm) results in the production of $(\text{NO})_m^-$ with $m \geq 2$ and $\text{NO}_2^-(\text{NO})_m$ with $0 \leq m \leq 2$. The photofragment yield spectra obtained for $n = 3$ –7 display a broad and structureless band profile with successive blue-shift with increase in the cluster size, indicating that N_3O_3^- (reference 1) behaves as a chromophoric core in the larger $(\text{NO})_n^-$. The observed fragmentation patterns suggest that photoexcitation of the N_3O_3^- chromophore is followed by direct dissociation into $(\text{NO})_2^-$, solvent evaporation to form $(\text{NO})_m^-$, and/or intracluster reactions to produce NO_2^- .

Reference

- 1) T. Tsukuda, M. Saeki, L. Zhu and T. Nagata, *Chem. Phys. Lett.* **295**, 416 (1998).