VIII-Q Structures and Photophysical Properties of Monolayer–Protected Metal Clusters

For the last decade, the monolayer-protected metal clusters (MPCs) have gained much attention both as prototype systems to study the size dependent evolution of the electronic properties of the metal clusters and as promising candidates for elementary units of nano-scale devices. The emergence of novel optical and electronic properties is expected for small-sized MPCs because their electronic energy levels become quantized due to the electron confinement into the small dimensions. For example, it is anticipated that the small MPCs exhibit photoluminescence since the radiative process of the photoexcited state can compete with the phonon-mediated nonradiative relaxation processes. Our interests are focused on the following issues on the MPCs: (1) preparation and characterization of the small MPCs 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), (3) development of size–selection method, and (4) clarification of the effects of the core size, core shape, and thiolate ligation on the optical and electronic properties.

VIII-Q-1 One-Pot Preparation of Subnanomerter-Sized Gold Clusters *via* Reduction and Stabilization by *meso*-2,3-Dimercaptosuccinic Acid

NEGISHI, Yuichi; TSUKUDA, Tatsuya

[*J. Am. Chem. Soc.* **125**, 4046–4067 (2003)]

We report herein a simple method to prepare subnanometer-sized gold clusters by the reactions between hydrogen tetrachloroaurate ($HAuCl_4$) and *meso*-2,3-dimercaptosuccinic acid (DMSA; $HO_2CCH(SH)CH(SH)CO_2H$) in water. It is demonstrated that DMSA molecules efficiently reduce the Au(III) species and stabilize the resultant gold clusters. The Au:DMSA clusters, which tend to aggregate into assemblages in water, can be well-isolated each other by ion-pair formation between the carboxyl groups of DMSA and tetraoctylammonium (TOA) cations. This surface modification enables us to examine the core size distributions of the individual clusters by mass spectrometry and TEM. It is revealed that the gold clusters comprised of 10–13 atoms (*ca.* 0.8 nm) are the main products of the reactions.

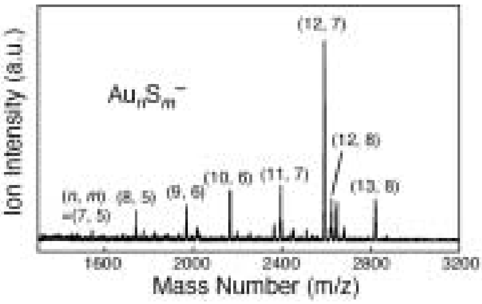

Figure 1. Laser desorption ionization mass spectrum of Au:DMSA-TOA clusters.

VIII-Q-2 Photoluminescence from Nearly Monodispersed Au_{12} Clusters Protected by *meso*-2,3-Dimercaptosuccinic Acid

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[*Chem. Phys. Lett.* **383**, 161–165 (2004)]

Nearly monodispersed gold clusters ($Au_{\sim 12}$) protected by *meso*-2,3-dimercaptosuccinic acid (DMSA) exhibit luminescence at 630 nm with a quantum yield of 1×10^{-6} upon the photoexcitation at 390 nm into the lowest electronic excited state. The large Stokes shift (1.2 eV) suggests that the visible PL is assigned to phosphorescence originating from a triplet-like excited state. The PL quantum yield was enhanced up to 0.9%, greater by 8 orders of magnitude than that of bulk gold, by thickening the protecting layer and freezing of the solvent at 77 K. The emission peak energy is discussed within the context of core-size dependent electronic structures by comparing with those of other gold MPCs reported in literatures.

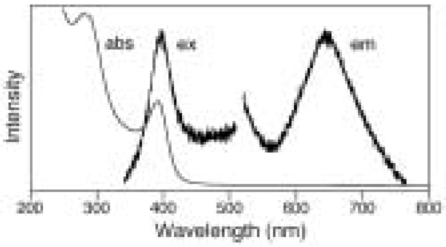

Figure 1. Optical absorption, emission and excitation spectra of Au:DMSA clusters at 298 K; λ_{ex} = 400 nm, λ_{em} = 630 nm.

VIII-Q-3 Isolation and Characterization of Subnanometer-Sized Gold Clusters

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The Au:SG clusters with the core diameters of 0.8–1.0 nm were synthesized in Kimura group by reducing $AuCl_4^-$ with $NaBH_4$ in the presence of glutathione GSH molecules ($AuCl_4^-$:GSH = 1:2).[1)] The Au:SG clusters thus prepared were further fractionated into five distinct components by using polyacrylamide gel electrophoresis (PAGE).[2),3)] In order to characterize the chemical composition of these components, the electrospray ionization (ESI) mass spectra were recorded by using an apparatus constructed at IMS. The negative-ion mode ESI mass spectra of these fractions are comprised of series of multiply charged ions of $Au_{21}(SG)_{12}$, $Au_{25}(SG)_{14}$, $Au_{28}(SG)_{16}$, $Au_{32}(SG)_{20}$, $Au_{38}(SG)_{23}$, respectively, demonstrating the isolation of nearly singly-sized clusters. It is found that these isolated clusters exhibit visible photoluminescence with quantum yields in the order of 10^{-3}.

References

1) S. H. Chen and K. Kimura, *Langmuir* **15**, 1075–1082 (1999).
2) T. G. Schaaff, G. Knight, M. N. Shafigullin, R. F. Borkman and R. L. Whetten, *J. Phys. Chem. B* **102**, 10643–10646 (1998).
3) T. G. Schaaff and R. L. Whetten, *J. Phys. Chem. B* **104**, 2630–2641 (2000).

VIII-Q-4 Construction of Apparatus for Photoelectron and Photodissociation Studies of Mass-selected Organometallic Clusters

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The electronic structures of the MPCs, especially in the subnanometer-sized regime, are significantly influenced by the thiolate (RS) coordination against the metallic cores as well as their core sizes. In order to study such effects, it is necessary to prepare and isolate the mass selected $M_n(SR)_m$ clusters ($m \geq 0$) in the gas phase, since the clusters with small m are unstable against the aggregation in liquid dispersion. To this end, we have developed a new apparatus, which consists of a cluster ion source, a tandem time-of-flight mass spectrometer, and a photoelectron spectrometer. In the cluster source, the bare metal clusters produced by laser vaporization of the metal target are allowed to react with the thiol molecules, RSH, to form organometallic clusters. The anionic clusters, $M_n(SR)_m^-$, are mass-selected by the first TOF mass spectrometer and then irradiated by pulsed laser light. The photoelectrons and photofragments are detected by the magnetic-bottle type photoelectron spectrometer and the secondary TOF mass spectrometer, respectively.

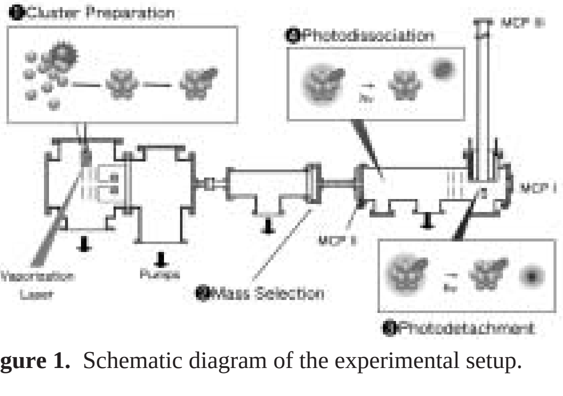

Figure 1. Schematic diagram of the experimental setup.

VIII-Q-5 EXAFS Study on Interfacial Structure between Pd Cluster and *n*-Octadecanethiolate Monolayer: Formation of Mixed Pd–S Interlayer

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[*Chem. Phys. Lett.* **376**, 26–32 (2003)]

The geometrical structure of a Pd cluster (diameter of ≈ 3.1 nm) protected by *n*-octadecanethiolate monolayer has been investigated by high-resolution TEM (HRTEM), XRD, and EXAFS spectroscopy. The HRTEM and XRD measurements have revealed that the cluster core is comprised of an *fcc* single crystal of Pd. The mean coordination numbers of the Pd–Pd and Pd–S shells determined by the Pd *K*-edge EXAFS analysis suggest that the surface of the Pd core is sulfurized to form a mixed Pd–S layer underneath the thiolate monolayer.

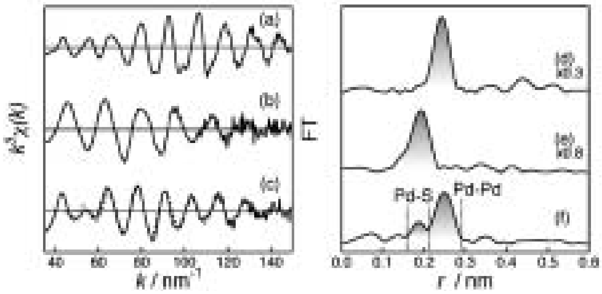

Figure 1. k^3-weighted Pd *K*-edge EXAFS spectra after background subtraction; (a) Pd foil, (b) PdS pellet, (c) Pd:SC_{18} clusters. The broken line in panel (c) represents the best-fit result. Fourier-transforms of the EXAFS spectra; (d) Pd foil, (e) PdS pellet, (f) Pd:SC_{18} clusters.

VIII-Q-6 Structures and Stabilities of Alkanethiolate Monolayers on Palladium Clusters as Studied by Gel Permeation Chromatography

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[*J. Phys. Chem. B* submitted]

Palladium clusters protected by a series of *n*-alkanethiolates, Pd:SC_n (SC_n = *n*-$C_nH_{2n+1}S$, n = 10, 12, 14, 16, and 18), were prepared by a ligand exchange approach: Pd clusters protected by poly (*N*-vinyl-2-pyrrolidone) (PVP) were transferred from aqueous phase to the toluene phase containing the thiols. The structures and stabilities of the thiolate monolayers of the Pd:SC_n clusters were investigated by gel permeation chromatography (GPC) together with TEM, XPS, and FT-IR. The thicknesses of the thiolate layers formed on the Pd clusters were evaluated from the differences between the hydrodynamic diameters and core diameters of the Pd:SC_n clusters, determined by GPC and TEM, respectively. The thicknesses thus obtained are in good agreement with the lengths of the corresponding thiolates in the all-*trans* conformations, illustrating that the alkanethiolates in nearly straight configurations are aligned almost perpendicularly to the core surfaces. Fractionation of the Pd:SC_{18} clusters by GPC yielded a series of the purified samples: the clusters in each fraction are different in their core sizes. The GPC measurements on the Pd:SC_n clusters with small n revealed the decomposition of the monolayers through spontaneous etching and their reconstruction by heat treatment in the presence of the free thiols. The mechanism of these processes is discussed. The present study demonstrates that the GPC provides an elemental and versatile means to characterize and purify the monolayer-protected clusters.

VIII-R Mass Spectroscopic Studies on Nanoscale Materials

Information on the size, shape, and dispersity is of fundamental importance in understanding natures and functions of nanoscale materials. Traditionally, transmission electron microscope (TEM) and powder X-ray diffraction have been employed to measure size, shape and size distributions of the nanoscale materials. We have applied an alternative technique, mass spectrometry, to provide more detailed insight into the structures of these fascinating materials.

VIII-R-1 Self-Assembly of Si Clusters into Single Crystal Arrangements: Formation of Si_{10} Cluster Crystals

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([1]Himeji Inst. Tech.; [2]GUAS)

[*Jpn. J. Appl. Phys.* **42**, L616–L618 (2003)]

Single crystals at an air/solution interface or a solution/hydrogen-terminated Si substrate interface were created using a self-assembly process, which originated from the hydrophobic nature of Si clusters. Mass analysis indicated that the components of the cluster crystals were partially oxidized hydrogenated Si_{10} clusters. At either interface the nearest-neighbor distances between lattice points in the Si cluster crystals were 0.53 nm or 0.60 nm, which is consistent with the diameters of the Si_{10} clusters. The slight difference in these values seems to be due to variations in the surface passivation of the component Si_{10} clusters.

VIII-R-2 Highly Oxygenated Fullerene $C_{60}O_n$ formed by Corona Discharge Ionization in the Gas Phase

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[*Chem. Phys. Lett.* in press]

Oxygenated fullerenes were produced by a vaporization source equipped with a corona discharge ionizer in the presence of a trace amount of oxygen. *In situ* mass analysis revealed that the species formulated as $C_{60}O_n$ ($n \leq 30$) are formed in the source and that the degree of oxygenation can be altered through the discharge current. Formation of the epoxidized structure in the $C_{60}O_n$ was confirmed by XPS measurements of the thin films of $C_{60}O_n$ and semi-empirical PM3 calculations for $C_{60}O_{30}$. The structures and formation processes for higher analogues $(C_{60})_mO_n$ (m = 2, 3) are briefly discussed.

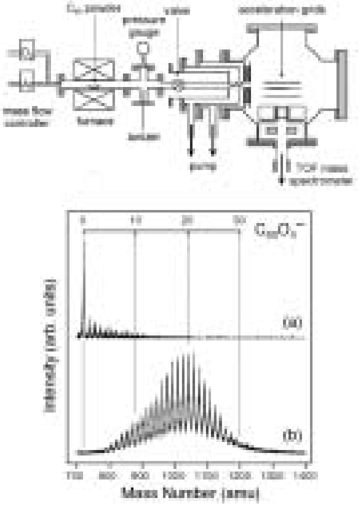

Figure 1. Schematic diagram of experimental setup (top) and typical mass spectra of the negative ions produced by the corona discharge ionizer (bottom) operated at 100 mA under Ar gas flow (a) without oxygen and (b) with 1% oxygen.

VIII-S Structures and Reactions of Molecular Cluster Ions

Molecular clusters, intermediate states of matter between the bulk and the molecule, provide us unique opportunities to study how the chemical and physical properties evolve with a degree of aggregation. We have studied reactions of hydrated anions with a simple molecule by using mass spectrometry, photoelectron and photodissociation spectroscopies and *ab initio* calculations.

VIII-S-1 Gas-Phase Reaction of Hydrated $CO_2^{\cdot -}$ Anion Radicals with CH_3I

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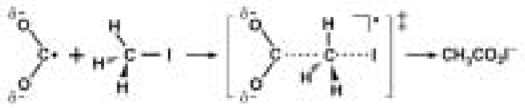
([1]Univ. Tokyo)

[*J. Phys. Chem. A* **107**, 8476–8483 (2003)]

Hydrated $CO_2^{\cdot -}$ anion radicals, $CO_2^{\cdot -}(H_2O)_n$, are selectively prepared in an electron-impact free jet of $CO_2^{\cdot -}$ containing H_2O. Mass spectrometric measurement reveals that $CO_2^{\cdot -}(H_2O)_n$ reacts with CH_3I to form an anion with $[(CO_2)(H_2O)]^-$ stoichiometry. The product $[(CO_2)(H_2O)]^-$ is further identified as the anion of acetyloxy iodide, $CH_3CO_2I^-$, based on the observation that $[(CO_2)(H_2O)]^-$ photodissociates at 532 nm into $CH_3CO_2^- + I$ or $CH_3CO_2 + I^-$ channels. The $CO_2^{\cdot -}(H_2O)_n + CH_3I$ reaction thus presents a sharp contrast to the corresponding reaction in solution: the gas-phase $CO_2^{\cdot -}(H_2O)_n$ behaves as a carboxylation reagent for alkyl halide (RX), whereas in aqueous solutions the reaction proceeds as $CO_2^{\cdot -} + RX \rightarrow CO_2 + R + X^-$. *Ab initio* calculations suggest that $CO_2^{\cdot -}(H_2O)_n$ can take on structures preferable for radical reactions: the hydraion occurs on the O atoms of $CO_2^{\cdot -}$ and the unpaired electron on the C atom remains uncovered with H_2O solvents. The reaction mechanism of the $CO_2^{\cdot -}(H_2O)_n + CH_3I$ process is discussed in conjunction with previous results of $(CO_2)_n^{\cdot -} + CH_3I$.[1)]

Reference

1) T. Tsukuda, M. Saeki, S. Iwata and T. Nagata, *J. Phys. Chem. A* **101**, 5103–5110 (1997).



Scheme 1.