IX-S 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-S-1 Magic-Numbered Au*n* Clusters Protected by Glutathione Monolayers (*n* = 18, 21, 25, 28, 32, 39): Isolation and Spectroscopic Characterization

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Small gold clusters (< 1 nm) protected by glutathione (GSH) monolayer were fractionated into six components by polyacrylamide gel electrophoresis (PAGE) and their chemical compositions were investigated by electrospray ionization (ESI) mass spectroscopy. The results demonstrate isolation of a series of magic-numbered gold clusters, $Au_{18}(SG)_{11}$, $Au_{21}(SG)_{12}$, $Au_{25\pm1}(SG)_{14\pm1}$, $Au_{28}(SG)_{16}$, $Au_{32}(SG)_{18}$, and $Au_{39}(SG)_{23}$. Their optical absorption spectra are highly structured with clear absorption onsets, which shift toward higher energies with reduction of the core size. These molecular-like gold clusters exhibit visible photoluminescence. The results reported herein provide helpful guidelines or starting points for further experimental and theoretical studies on structures, stabilities and optical properties of small gold MPCs.

IX-S-2 Effect of Thiolate Ligation on Stabilization and Electronic Structures of Subnanometer-Sized Gold Clusters

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Small gold clusters protected by *N*-(2-mercaptopropionyl)glycine (MPG) and mercaptosuccinic acid (MSA) were prepared and isolated into several components by high-resolution PAGE. Mass analysis shows that the core sizes of the monolayer-protected gold clusters (gold MPCs) preferentially formed are dependent on the thiolate structures. This finding suggests the completion of the protecting shell plays an important role in stabilizing the gold MPCs with specific core sizes. In other words, it may be possible to prepare gold MPCs with any desired core size by proper design of the thiolate structures. Remarkable effect of thiolate ligation on the optical properties offers a new strategy toward fine-tuning of the fundamental properties of the MPCs through the degree of thiolate ligation as well as core size.

IX-S-3 Construction of Apparatus for Photodissociation and Surface-Induced Dissociation Studies of MPCs

NEGISHI, Yuichi; TSUKUDA, Tatsuya

Photo-dissociation and surface-induced dissociation of MPCs provide direct information on their thermodynamic stabilities. Such information also helps in the understanding of the origin of the preferential formation of certain-sized MPCs. Thus, we have improved our ESI-TOF mass spectrometer by introducing two components: a quadrupole ion trap and a reflectron coupled with an in-line MCP detector with a center hole. The continuous beam of the MPC ions formed in the ESI source is guided to the quadrupole ion trap. The ions accumulated in the trap are extracted into a primary TOF mass spectrometer typically operated at 10 Hz. The mass-selected cluster ions are irradiated by a pulsed laser or allowed to collide with the solid surface mounted at the end of the reflectron. The fragment ions generated are detected by a secondary TOF mass spectrometer.

IX-S-4 Construction of Low-Temperature Optical Spectroscopy System

NEGISHI, Yuichi; TSUNOYAMA, Hironori; TSUKUDA, Tatsuya

We have demonstrated that subnanometer-sized gold clusters exhibit clear structures in their optical spectra even at room temperature. In order to minimize the influence from vibration excitation of internal modes and/or isomers (if present), the measurement at low temperature is required. The system under construction is composed of a sample holder supported on a cold head (~22 K), a vacuum chamber, and a turbo-molecular pump. The system can be coupled to a spectrophotometer (HITACHI, U-2010) or a spectrofluorometer (JASCO, FP-6600) to obtain optical data of the neat film of the clusters.

IX-S-5 Heat Induced Long-Range Ordering of Small Gold Nanoparticles with Tunable Interparticle Spacings

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The monodisperse Au nanoparticles smaller than 2 nm were prepared by the reduction of $HAuCl_4 \cdot 4H_2O$ in DMF/H_2O in the presence of a series of ligands, 2,6-bis(1’-(*n*-thioalkyl)benzimidazol-2-yl)pyridine (TC_nBIP, n = 8, 10, 12), and formed hexagonal close packed (*hcp*) two-dimensional (2D) superlattices with tunable interparticle spacings from 1.9 to 2.5 nm by the ligand length. Then we present the new methodology to fabricate the long range ordered 2D superlattices of 1.5-nm Au nanoparticles at the air-water interface, which includes a heat-induced rearrangement of *hcp* domains into long range ordered *hcp* superlattices stabilized by interligand π-π interaction. The large-scale *hcp* 2D superlattices of 1.5-nm Au nanoparticles were obtained, and advantageously transferable onto any substrate.

IX-S-6 Colloidal Gold Nanoparticles as Catalyst for Carbon–Carbon Bond Formation: Application to Aerobic Homocoupling of Phenylboronic Acid in Water

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Gold nanoparticles (ϕ < 2 nm) stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP NPs) were prepared by reduction of $AuCl_4^-$ with $NaBH_4$ in the presence of PVP and characterized via array of methods including optical absorption spectroscopy, TEM, XRD, XANES, EXAFS, and XPS. It is found for the first time that the Au:PVP NPs act as catalyst toward homocoupling reactions of phenylboronic acid in water under aerobic conditions. Suppression of the biphenyl formation under anaerobic condition indicates that molecular oxygen dissolved in water is intimately involved in the coupling reactions. Effect of the particle size and the PVP coordination upon the catalytic activity is discussed.

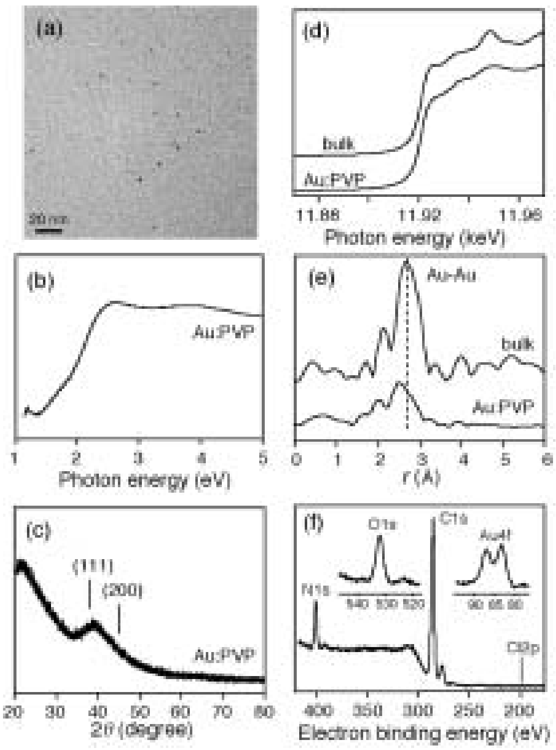
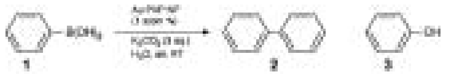


Figure 1. (a) TEM image, (b) optical absorption spectrum, (c) XRD profile, (d) Au L_3-edge XANES, (e) FT-EXAFS, (f) XPS of Au:PVP(K-30).

Table 1. Homocoupling Reactions of Phenylboronic Acid in Water Catalyzed by Au:PVP NPs[a].



entry	catalyst	yield (%)[b]			d (nm)[d]
		1[c]	**2**	**3**	
1	Au:PVP(K-15)	16	62	22	3.1±0.7
2	Au:PVP(K-30)	3	72	23	2.9±0.4
3	Au:PVP(K-90)	trace	64	35	3.1±0.5
4[e]	Au:PVP(K-30)	>99	trace	trace	–
5	recovered from #2[f]	26	61	13	3.4±0.5
6	recovered from #5[f]	43	49	8	3.4±0.6

[a]The reactions were carried out at room temperature under air for 24 h. [b]Estimated from NMR analysis. [c]Detected as anhydride. [d]Particle diameter after the reaction determined by TEM measurement. [e]The reaction was carried out under nitrogen. [f]The Au:PVP NPs were collected by centrifugal ultrafiltration by a filter with10 kDa cutoff.

IX-S-7 Fabrication of Model Catalytic System by Use of Monolayer-Protected Metal Clusters as Precursor

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Metal clusters supported on a surface have been regarded as an ideal model for the study of heterogeneous catalysts.1) In these studies, metal clusters with a given size were softly deposited on the surface, and the catalytic activity was investigated as a function of the cluster size. However, following difficulties are encountered in this approach: (1) the clusters tend to aggregate at high coverage, (2) the structures of the clusters deposited on a surface may not be uniform because of isomers present in the beam or surface-induced structural rearrangement. In order to circumvent these difficulties, we have been developing a new scheme to fabricate an ordered array of size-selected metal clusters. An ordered array of size-selected MPCs is transferred to a solid substrate by using a Langmuir-Brodgett technique. As an initial step, we prepared the monolayer of alkanethiolate-protected gold clusters on a carbon-coated copper grid. In the monolayer obtained, the gold MPCs are arranged regularly with interparticle distance determined by the thickness of the thiolate monolayer.2) The substrate is subsequently transferred into a UHV chamber which accommodates a magnetron-type plasma source. The organic layer of the MPCs is etched by exposure of the oxygen and/or hydrogen plasma. The structures of the resulting clusters are characterized by XPS and AFM. The activity of the model catalysts thus prepared is investigated in situ by means of thermal desorption spectroscopy.

References

1) A. Sanchez, S. Abbet, U. Heiz, W. -D. Schneider, H. Hakkinen, R. N. Barnett and U. Landman, *J. Phys. Chem. A* **103**, 9573 (1999).
2) P. Liljeroth, D. Vanmaekelbergh, V. Ruiz, K. Kontturi, H. Jiang, E. Kauppinen and B. M. Quinn, *J. Am. Chem. Soc.* **126**, 7126 (2004).