JOURNAL OF
Materials
CHEMISTRY
Communication

Highly reactive intermediate-functionalized gold clusters: synthesis and immobilization on silica supports through amide-forming coupling

Kensuke Akamatsu,*[a] Jun Hasegawa,[a] Hidemi Nawafune,*[a] Hiroyuki Katayama[b] and Fumiyuki Ozawa[b]

[a]*Faculty of Science and Engineering, High Technology Research Center, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan. E-mail: akamatsu@center.konan-u.ac.jp*
[b]*Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan*

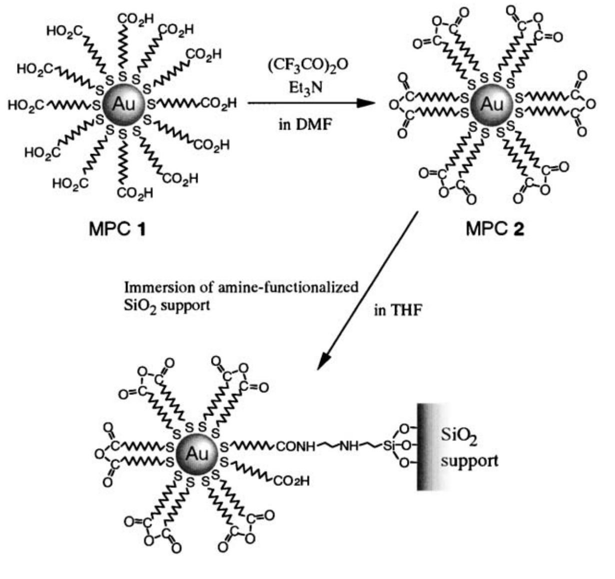
Received 23rd July 2002, Accepted 19th August 2002
First published as an Advance Article on the web 27th August 2002

Gold clusters functionalized with interchain carboxylic anhydride over their entire surface have been successfully immobilized on amine-functionalized silica supports through amide-forming coupling, providing ordered two-dimensional arrangements of cluster monolayers, which might find utility in the development of artificial nanostructures for nanoelectronic device applications.

Composite nanostructures consisting of metal clusters and solid-state matrices have recently attracted much attention and are considered to be a potential class of materials for future nanodevice applications based on novel functions arising from size-quantization effects.[1] In particular, monolayer-protected gold clusters (Au-MPCs) have been the subject of intense study with respect to the fabrication of cluster-based structures as part of the development of artificial nanostructured materials.[2] More recently, these structures have been recognized as potentially useful in nanoelectronic applications, on the basis of Coulomb charging effects.[3]

Surface modification of the clusters and their immobilization on an appropriate solid support, such as metals, dielectric materials, or semiconductors, is an indispensable technology for practical applications of MPCs in nanodevices. A wide variety of methods for the fabrication of Au-MPC-based structures have been reported. Most studies have focused on the immobilization of clusters on the support through self-assembly,[2a,2b,2d,2g,3a,4] electrostatic interaction,[2f,5] complexation,[6] molecular linking,[7] and/or covalent bonding.[2h,8] Among these, non-covalent bond-mediated immobilization is considered to be stable only under specific conditions due to the relatively weak interaction, effectively limiting the range of applications for this approach. Although the covalent bond-mediated immobilization of clusters may be suitable for various applications with regard to stability, there have been, as yet, few studies on the topic. Gold cluster deposition on self-assembled monolayers bearing mercapto groups provides immobilization of the clusters through simple covalent bonding (typically alkyl chains).[2h,8a,8b] In this case, however, underivatized Au clusters are necessary for immobilization, for which the preparation of very small clusters (<2 nm) is generally difficult. Recently, Chan and Yu reported the immobilization of Au-MPCs through stable oximes formed by chemoselective ligation, but no direct evidence for covalent bonding was presented.[8c] There remains a need for the development of a facile process for stable chemical immobilization of clusters on supports.

Herein, we describe an experimental study involving a new approach for the synthesis of Au clusters functionalized with a highly reactive intermediate and the immobilization of these clusters onto a silica support. The immobilization is mediated by covalent bond formation, which utilizes an amide-forming coupling reaction between carboxylic anhydride introduced on the surface of the Au clusters and amine groups attached to the silica support (Scheme 1). The procedure involves the synthesis of Au clusters functionalized with a carboxylic acid monolayer (MPC **1**), followed by transformation of these protective molecules into interchain carboxylic anhydride by treatment with trifluoroacetic anhydride, as applied to self-assembled monolayers on gold substrates.[9] The anhydride-protected Au clusters (MPC **2**) are then reacted with amino groups on a thin silica film and/or a colloid, uniformly immobilizing the Au clusters as a monolayer through covalent bonding. In this reaction, carboxylic anhydride, chosen as the functional molecules for Au clusters, and the amine group on the support react directly in a facile, predictable and reproducible manner to form stable amide bonds in high yield without protection or derivatization of these pairs of functional groups.



Scheme 1 Schematic illustration of proposed transformation from carboxylic acid-functionalized Au clusters (**1**) to interchain carboxylic anhydride-functionalized Au clusters (**2**) and subsequent immobilization on amine-functionalized silica supports through an amide-forming coupling reaction.

DOI: 10.1039/b207167c

This journal is © The Royal Society of Chemistry 2002

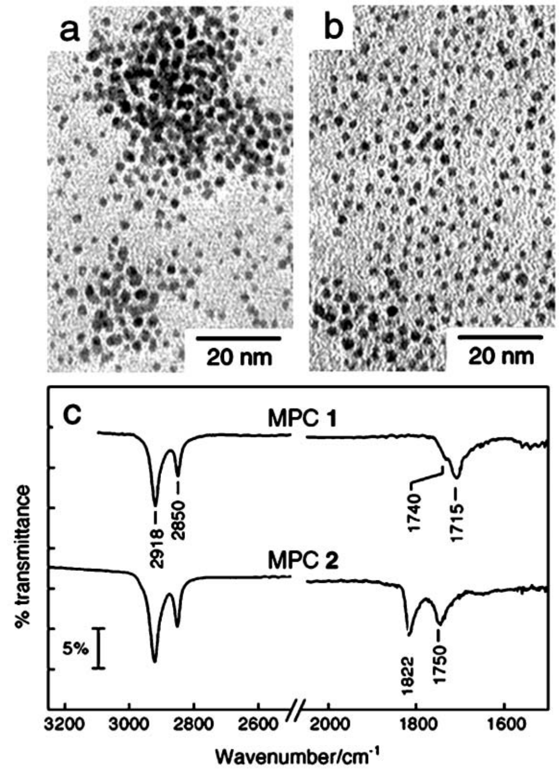


Fig. 1 TEM images of (a) MPCs **1** and (b) MPCs **2**, and (c) FT-IR spectra of these clusters, showing clean transformation from carboxylic acid to interchain carboxylic anhydride on the Au clusters. TEM samples were prepared by dropping a small amount of THF solution containing the Au clusters onto carbon-coated TEM copper grids.

MPCs **1** were prepared according to the method reported by Brust *et al.*[10] using 11-mercaptundecanoic acid as the stabilizing agent.[11] Transmission electron microscopy (TEM) revealed a mean diameter of 1.9 nm (standard deviation = 0.33 nm) for MPCs **1** [Fig. 1(a)]. These clusters are observed to form a number of aggregates on a carbon thin film supported on a TEM grid, presumably due to the formation of carboxylic acid dimers between neighboring Au clusters. For preparation of MPCs **2**, a solution containing MPCs **1** (30 mg, *ca.* 4.7×10^{-2} mmol of –CO$_2$H) in DMF (15 mL) was added to a freshly prepared solution of trifluoroacetic anhydride (1.4 mL, 9.9 mmol) and triethylamine (2.8 mL, 20 mmol) in DMF (45 mL) under argon. After this mixture was stirred at room temperature for 1 h, volatile materials were removed by distillation at 40 °C under reduced pressure. The oily residue was slowly added to vigorously stirred water (800 mL, distilled) to give a black precipitate, which was then collected by filtration, washed with copious amounts of water, and dried under vacuum. TEM observation of MPCs **2** reveals a uniform two-dimensional dispersion of clusters, confirming that there is no significant aggregation of these clusters [Fig. 1(b)].

The surface structural features of the present Au clusters are characterized by surface-bound carboxylic acid functionality. The Fourier transform infrared (FT-IR) spectrum for MPCs **1** [Fig. 1(c)] shows a band attributed to the backbone modes of alkyl chains, together with a C=O stretching band at 1715 cm^{-1} with a shoulder at 1740 cm^{-1}, assigned to hydrogen-bonded and free carboxylic acids, respectively.[12] The relatively high intensity of the signal assigned to the hydrogen-bonded carbonyl groups reflects the presence of head-to-head hydrogen bonding between neighboring MPCs **1** (inter-shell dimer formation),[4d] which leads to the formation of aggregates, as seen in Fig. 1(a).

After treatment with trifluoroacetic anhydride and triethylamine (MPCs **2**), the spectrum in the C–H stretching region remain unchanged, while new bands were observed, corresponding to C=O asymmetric (1822 cm^{-1}) and symmetric (1750 cm^{-1}) stretching modes of carboxylic anhydride. These bands arise from intramolecular coupling between the carbonyl vibrations in in-phase and out-of-phase modes.[13] Most importantly, the complete disappearance of all carboxylic acid C=O stretching bands indicates that the reaction of carboxylic acids with trifluoroacetic anhydride proceeds cleanly. The peak position and relative intensity of these stretching bands are characteristic of acyclic anhydrides,[13b] and the changes in the IR spectra after treatment of **1** with trifluoroacetic anhydride are similar in form to those observed for self-assembled monolayers of 16-mercaptohexanoic acids and their anhydrides on a flat Au substrate.[9a] Preliminary X-ray photoelectron spectroscopy measurements for MPCs **2** revealed no sign of the presence of trifluoroacetyl moieties, and no aggregates appeared in the TEM image [Fig. 1(b)]. This indicates that the carboxylic anhydrides are derived from the reaction of two adjacent carboxylic acid moieties attached to one Au core, and not from carboxylic acid and trifuluoroacetic acid or the interconnection of two carboxylic acids attached to neighboring Au cores.

The reaction of MPCs **2** with *n*-butylamine in THF for 10 min resulted in the formation of Au clusters protected by a mixed monolayer comprised of a mixture of carboxylic acids and alkylamides (results not shown) on the Au core.[14] This demonstrates the extremely high reactivity of MPCs **2** with respect to the amide-forming coupling reaction. This type of reaction is rapid and can be used for immobilization on amine-functionalized silica supports.[15] Representative results are shown in Fig. 2. The TEM image in Fig. 2(a) confirms that the Au clusters are successfully immobilized on the silica thin film after immersion of the film in THF containing MPCs **2** (reaction time: 20 min). Most of the clusters are isolated individually to form an ordered two-dimensional hexagonal arrangements of the Au cluster monolayer on the silica surface. Several defects are seen in the image, which could be due to the size distribution of the clusters. The Fourier transformation of the image [inset in Fig 2(a)] displays spots with spacings

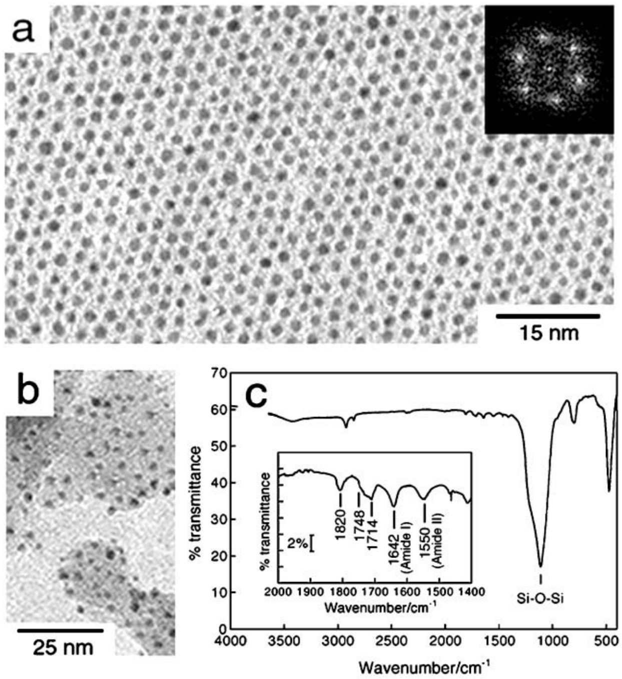


Fig. 2 TEM images of MPCs **2** immobilized on (a) a silica thin film (inset: Fourier transform of the TEM image) and (b) colloids. (c) FT-IR spectrum of MPCs **2** immobilized on silica colloids and enlargement (inset) of the 1400 to 2000 cm^{-1} region.

corresponding to the separations of ordered planes comprised of Au clusters, supporting the long-range ordering in the cluster monolayer. Although ordered arrangements of metal clusters were reported for ligand-stabilized Au clusters on a polymer-modified surface through acid–base interaction,[2f] the present results can be considered as the first successful immobilization of Au clusters in ordered two-dimensional form mediated by a covalent bond-forming reaction. The almost complete organization area was dependent on experimental conditions; a detailed study related to the organization mechanism for the anhydride-protected Au clusters is in progress and the results will be presented elsewhere.

Direct evidence for the amide-forming reaction has been obtained from FT-IR measurements on Au clusters immobilized on silica colloids, the results of which are shown in Fig. 2(b) and (c). After mixing, with stirring, a THF solution containing MPCs **2** and amine-functionalized silica colloids, precipitation took place within 5 min. TEM observation of the obtained precipitates revealed that each silica colloid is surrounded by a number of Au clusters, which are sometimes attached to neighboring silica colloids [Fig. 2(b)].[16] The peaks observed at 1642 and 1550 cm^{-1} in the IR spectrum of these precipitates [inset of Fig. 2(c)] are assigned to the amide I (C=O stretching) and amide II (N–H bending) modes of the amide bond.[17] Other characteristic peaks can be seen, which arise from the remaining carboxylic anhydride (1820 and 1748 cm^{-1}) and carboxylic acids formed by the coupling reaction (1714 cm^{-1}). These results indicate that the immobilization of Au clusters arises from the amide-forming coupling reaction. The chemical bond thus formed between the Au clusters and the support prevents the Au clusters from being removed by, for example, repeated washing under ultrasonication. As the amide I and II modes are predominantly conformationally sensitive to local order related to the structural arrangement of carbonyl groups,[17] a detailed analysis of the spectrum of the amide mode is currently being made in order to verify the local structure of the interface between Au clusters and the silica support.

In conclusion, the trifluoroacetic anhydride-promoted reaction presented here allows clean transformation from the carboxylic acid moieties attached to Au clusters to interchain carboxylic anhydride. The highly reactive intermediate introduced uniformly over the entire cluster surface provides direct and rapid immobilization of Au clusters as a two-dimensional hexagonally close-packed monolayer on amine-functionalized silica substrates through an amide-forming coupling reaction. This process can also be extended to the preparation of patterned architectures and three-dimensional superstructures, and is applicable for immobilization of the clusters on various kinds of supports, including complex shapes and large surface areas. Additionally, these clusters allow facile modification of the cluster surface with other types of functionality (*e.g.* fluorophores, biomolecules) with a controlled structure through the appropriate choice of molecules, even after immobilization, because anhydrides remain on the cluster surface after immobilization. Potential applications for this approach are currently being investigated.

Acknowledgement

The authors would like to acknowledge K. Toshikiyo for help with the transmission electron microscopy observations.

Notes and references

1 (*a*) *Clusters and Colloids*, ed. G. Schmid, VCH, Weinheim, 1994; (*b*) *Nanoscale Materials in Chemistry*, ed. K. J. Klabunde, John Wiley & Sons, Inc., New York, 2001.

2 (*a*) R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney and R. G. Osifchin, *Science*, 1996, **273**, 1690; (*b*) C. J. Kiely, J. Fink, M. Brust, D. Bethell and D. J. Schiffrin, *Nature*, 1998, **396**, 444; (*c*) G. Schmid, *J. Chem. Soc., Dalton Trans.*, 1998, 1077; (*d*) Z. L. Wang, *Adv. Mater.*, 1998, **10**, 13; (*e*) A. J. Boal, F. Ilhan, J. E. DeRouchey, T. Thurn-Albrecht, T. P. Russell and V. M. Rotello, *Nature*, 2000, **404**, 746; (*f*) G. Schmid, M. Bäumle and N. Beyer, *Angew. Chem., Int. Ed.*, 2000, **39**, 181; (*g*) J. E. Martin, J. P. Wilcoxon, J. Odinek and P. Provencio, *J. Phys. Chem. B.*, 2000, **104**, 9475; (*h*) H. X. He, H. Zhang, Q. G. Li, T. Zhu, S. F. Y. Li and Z. F. Liu, *Langmuir*, 2000, **16**, 3846; (*i*) T. O. Hutchinson, Y.-P. Liu, C. Kiely, C. J. Kiely and M. Brust, *Adv. Mater.*, 2001, **13**, 1800; (*j*) T. Yonezawa, S. Onoue and N. Kimizuka, *Langmuir*, 2001, **17**, 2291; (*k*) C. R. Mayer and S. Neveu. V. Cabuil, *Adv. Mater.*, 2002, **14**, 595.

3 (*a*) G. Markovich, D. V. Leff, S.-W. Chung, H. M. Soyez, B. Dunn and J. R. Heath, *Appl. Phys. Lett.*, 1997, **70**, 3107; (*b*) M. Y. Han, L. Zhou, C. H. Quek, S. F. Y. Li and W. Huang, *Chem. Phys. Lett.*, 1998, **287**, 47; (*c*) D. I. Gittins, D. Bethell, D. J. Schiffrin and R. J. Nichols, *Nature*, 2000, **408**, 67; (*d*) D. I. Gittins, D. Bethell, R. J. Nichols and D. J. Schiffrin, *J. Mater. Chem.*, 2000, **408**, 67; (*e*) G. Schmid and Y.-P. Liu, *Nano Lett.*, 2001, **1**, 405; (*f*) S. Chen and R. Pei, *J. Am. Chem. Soc.*, 2001, **123**, 10607.

4 (*a*) R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke and U. Landman, *Adv. Mater.*, 1996, **8**, 428; (*b*) S. Chen, *J. Phys. Chem. B.*, 2000, **104**, 664; (*c*) T. Teranishi, M. Haga, Y. Shiozawa and M. Miyake, *J. Am. Chem. Soc.*, 2000, **122**, 4237; (*d*) W. Zheng, M. M. Maye, F. L. Leibowitz and C. J. Zhong, *Anal. Chem.*, 2000, **72**, 2190.

5 (*a*) T. Yonezawa, S. Onoue and T. Kunitake, *Adv. Mater.*, 1998, **10**, 414; (*b*) J. Schmitt, P. Mächtle, D. Eck, H. MöHwald and C. A. Helm, *Langmuir*, 1999, **15**, 3256; (*c*) T. Yonezawa and T. Kunitake, *Colloids Surf., A*, 1999, **149**, 193; (*d*) F. Auer, M. Scotti, A. Ulman, R. Jordan, B. Sellergren, J. Garno and G.-Y. Liu, *Langmuir*, 2000, **16**, 7554; (*e*) T. H. Galow, A. K. Boal and V. M. Rotello, *Adv. Mater.*, 2000, **12**, 576; (*f*) M. M. Maye, J. Luo, L. Han and C.-J. Zhong, *Nano Lett.*, 2001, **1**, 575.

6 (*a*) W. P. Wuelfing, F. P. Zamborini, A. C. Templeton, X. Wen, H. Yoon and R. W. Murray, *Chem. Mater.*, 2001, **13**, 87; (*b*) J. F. Hicks, F. P. Zamborini, A. J. Osisek and R. W. Murray, *J. Am. Chem. Soc.*, 2001, **123**, 7048.

7 (*a*) K. G. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735; (*b*) K. G. Grabar, K. B. Brown, C. D. Keating, S. J. Stranick, S.-L. Tang and M. J. Natan, *Anal. Chem.*, 1997, **69**, 471; (*c*) T. A. Taton, R. C. Mucic, C. A. Mirkin and R. L. Latsinger, *J. Am. Chem. Soc.*, 2000, **122**, 6305; (*d*) L. M. Demers, S.-J. Park, T. A. Taton, Z. Li and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 3071.

8 (*a*) M. Brust, D. Bethell, C. J. Kiely and D. J. Schiffrin, *Langmuir*, 1998, **14**, 5425; (*b*) N. Fishelson, I. Shkrob, O. Lev, J. Gun and A. D. Modestov, *Langmuir*, 2001, **17**, 403; (*c*) E. W. L. Chan and L. Yu, *Langmuir*, 2002, **18**, 311.

9 (*a*) L. Yan, C. Marzolin, A. Terfort and G. M. Whitesides, *Langmuir*, 1997, **13**, 6704; (*b*) E. Ostuni, R. C. Chapman, R. E. Holmlin, S. Takayama and G. M. Whitesides, *Langmuir*, 2001, **17**, 5605.

10 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.

11 A typical experimental procedure is as follows: a solution of tetraoctylammonium bromide (328 mg, 0.60 mmol) in toluene (40 mL) was added to an aqueous solution of $HAuCl_4{\cdot}4H_2O$ (15 mM, 20 mL, 0.30 mmol). A solution of 11-mercaptoundecanoic acid (65.5 mg, 0.3 mmol) in toluene (10 mL) was then gradually added to the resulting mixture while stirring vigorously, followed by dropwise addition of a freshly prepared aqueous solution of $NaBH_4$ (0.30 M, 10 mL, 3.0 mmol). After stirring the mixture for 3 h, the organic layer was separated, washed with distilled water (3 × 100 mL), and concentrated to dryness under reduced pressure. The black solid thus obtained was washed ultrasonically with chloroform and filtered off to give the desired Au clusters. Thermogravimetric analysis revealed that the organic component of the product amounted to 33.7 wt%.

12 R. G. Nuzzo, L. H. Dubois and D. L. Allara, *J. Am. Chem. Soc.*, 1990, **112**, 558.

13 (*a*) R. G. Cooke, *Chem. Ind.*, 1995, 142; (*b*) W. G. Dauben and W. W. Epstein, *J. Org. Chem.*, 1959, 1595.

14 The procedure for the reaction of MPCs **2** with *n*-butylamine is as follows: to the THF solution containing MPCs **2** was added an excess amount of *n*-butylamine (relative to the carboxylic anhydride moieties). After stirring the mixture at room temperature for 20 min, the solvent and remaining *n*-butylamine were

evaporated under vacuum. FT-IR spectroscopy confirmed the formation of amide bonds (1640 and 1550 cm^{-1}) and carboxylic acid (1738 cm^{-1}).

15 The SiO_2 supports used are sputtered SiO_2 thin films (20 nm in thickness) coated on a TEM grid and SiO_2 colloids (15 nm in average diameter), both of which are functionalized with *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane by silane coupling reaction. The freshly prepared anhydride-functionalized Au clusters were dissolved in THF (*ca.* 30 mL) and used immediately for subsequent immobilization on silica supports.

16 The procedure for immobilization of the clusters on SiO_2 colloids is as follows: a THF solution containing excess amount of the colloids was added to the solution containing a small amount of the anhydride-functionalized Au clusters, providing network aggregates consisting of SiO_2 colloids linked by Au clusters through amide bonds, which are detectable by FT-IR spectroscopy.

17 (*a*) S. Krimm, *Biopolymers*, 1983, **22**, 217; (*b*) D. J. Skrovanek, S. E. Howe, P. C. Painter and M. M. Coleman, *Macromolecules*, 1986, **19**, 699.