

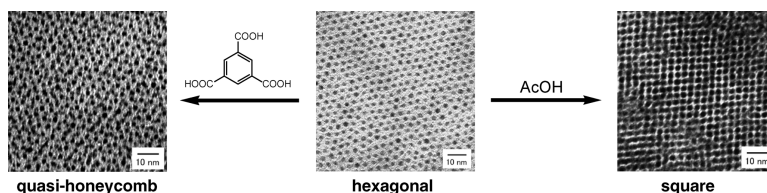
Communication

Formation of Low-Symmetric 2D Superlattices of Gold Nanoparticles through Surface Modification by Acid–Base Interaction

Masayuki Kanehara, Yasunori Oumi, Tsuneji Sano, and Toshiharu Teranishi

J. Am. Chem. Soc., **2003**, 125 (29), 8708–8709 • DOI: 10.1021/ja035187j • Publication Date (Web): 24 June 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 15 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Formation of Low-Symmetric 2D Superlattices of Gold Nanoparticles through Surface Modification by Acid–Base Interaction

Masayuki Kanehara,[†] Yasunori Oumi,[†] Tsuneji Sano,[†] and Toshiharu Teranishi^{*,†,‡}

School of Materials Science, Japan Advanced Institute of Science and Technology and “Organization and Function”, PRESTO, Japan Science and Technology Corporation, 1-1 Asahidai, Tatsunokuchi, Nomi, Ishikawa 923-1292, Japan

Received March 16, 2003; E-mail: tosiharu@jaist.ac.jp

Fabrication of ordered metal nanoparticles with well-defined two-dimensional (2D) configuration would enable us to produce novel optical and nanoelectronic devices. One of the most straightforward approaches for construction of 2D superlattices is a self-assembly, whereby a colloidal solution of chemically stabilized nanoparticles is placed on a substrate surface and the solvent is allowed to evaporate in a controlled fashion. The formation of 2D superlattices^{1–9} and one-dimensional chains^{10,11} has been vigorously investigated. Recently, extensive studies have been performed on optical¹² and electronic^{13–15} properties of 2D superlattices of metal nanoparticles, and it has been proposed that the structure,¹⁴ interparticle spacing,^{12,15,16} and periodicity¹⁷ of 2D superlattices greatly affect their properties. The symmetry of the 2D superlattice also has a potential to control its electric conductivity and optical property. For the production of future Ultra Large Scale Integration (ULSI), elucidation of electron transport behaviors in well-ordered 2D superlattices of metal nanoparticles with different symmetries is of great importance. The regularly hexagonal close-packed (hcp) 2D superlattices are well established, and several groups have succeeded in ordering metal nanoparticles into 2D superlattice with low-symmetric structures, such as square structure.^{9,18–20} In this work we demonstrate, for the first time, that different symmetric structures of 2D superlattices can be obtained from the same gold nanoparticles protected by amino-derivatized ligands through surface modification with the different kinds of organic acids.

To obtain a general means for low-symmetric 2D superlattices of nanoparticles, we have synthesized a newly designed protective agent, bis-4,4'-(4,4'-dithiobutylbenzyl)-*N,N,N',N'*-tetraethylamine (TBA, see inset in Figure 1 and Supporting Information for detailed synthetic procedure and characterization data), in which a disulfide group serves to coordinate to the gold surface, benzene rings endow Au nanoparticles with solvility for organic solvents, and amino groups form ammonium salts with organic acids to control the structure of 2D superlattice.

The Au nanoparticles were prepared using TBA as a protective agent. One milliliter of a 10 mM *N,N*-dimethylacetamide (DMAc) solution of HAuCl₄·4H₂O (10 μmol) was added to the mixture of 5 μmol of TBA in DMAc (44 mL). Under vigorous stirring, 0.1 mmol of NaBH₄ in methanol (5 mL) was added to the solution. After additional stirring for 30 min, the color of the solution turned brown. The nanoparticles were precipitated with water (~50 mL), filtered, and washed several times with a methanol/water (2:1, vol/vol) mixed solvent. The TBA-protected Au (TBA-Au) nanoparticles were 2.4 ± 0.2 nm in size and showed good solvility, not only for nonpolar solvents such as toluene but also for polar solvents such as ethyl acetate and DMAc. After the precipitate was redispersed into 5 mL of ethyl acetate, the Au nanoparticles were neutralized

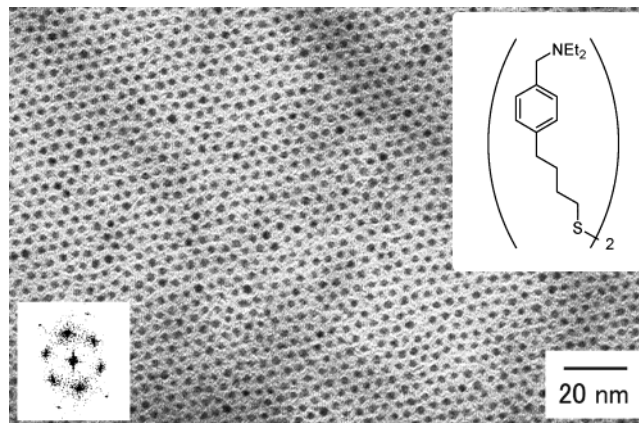


Figure 1. TEM image of 2D superlattice of TBA-Au nanoparticles. The insets on the right and left show the chemical structure of the TBA ligand and a FFT image of superlattice, respectively.

with organic acid, 1,3,5-benzenetricarboxylic acid (BTCA) or acetic acid (AcOH), to endow the Au nanoparticles with good solvility for water (see Supporting Information for more details). These nanoparticle aqueous solutions were then put on a polyvinyl formal-coated copper grid, and the solvent was slowly evaporated to obtain the low-symmetric 2D superlattices. Adding ethylene glycol lowers the evaporation rate and improves the affinity of the solution to the grid, leading to an expansion of the organized area of the 2D superlattice. A similar effect of addition of dodecanethiol to a solution of dodecanethiol-protected Au nanoparticles was reported by Lin et al.⁵

Figure 1 shows the TEM image of a hcp 2D superlattice of the TBA-Au nanoparticles, obtained by a slow evaporation of the toluene solution on an amorphous carbon-coated copper grid. The mean interparticle spacing was estimated to be ~1.4 nm, which was obtained by a direct measurement of individual spacings within well-ordered hcp domain. By taking the length of the TBA molecule as ~1.3 nm into consideration, this result suggests that each Au nanoparticle is stabilized by one TBA layer, and presumably the TBA ligands are interpenetrating each other as a result of a π - π interaction between benzene rings of adjacent particles (Supporting Information, Figure S1a).

Compared with this hcp superlattice, similar hcp (Figure 2a) and quasi-honeycomb (Figure 2b) superlattices were obtained from the solution of TBA-BTCA salt-protected Au (TBA-BTCA-Au) nanoparticles. In Figure 2a, the mean interparticle separation in the hcp superlattice was 3.0 nm, well corresponding to the sum of two TBA layers and one BTCA molecule. Hydrogen bonds between TBA molecules and interparticle Coulomb repulsion caused by ammonium salt formation on the surface of the nanoparticles would be responsible for the formation of hcp structure (Supporting Information, Figure S1b).

[†] Japan Advanced Institute of Science and Technology.

[‡] Japan Science and Technology Corporation.

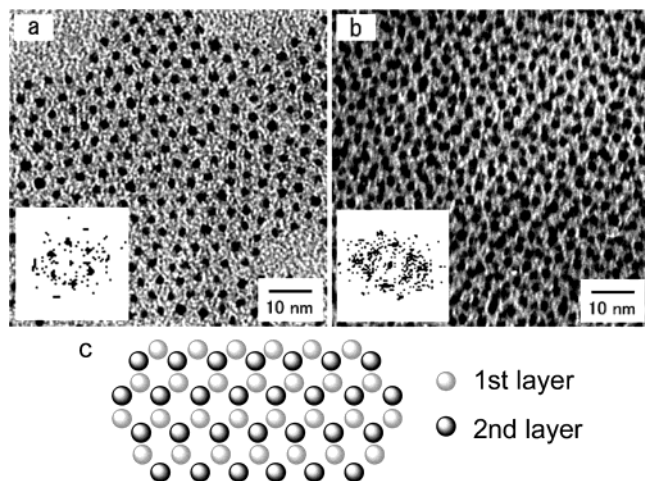


Figure 2. TEM image of TBA-BTCA-Au nanoparticles with (a) hcp and (b) quasi-honeycomb structures. (c) Schematic illustration of the bilayer structure of quasi-honeycomb structure. The insets show FFT images.

When another hcp layer was placed on the already-formed hcp layer, the 3-fold quasi-honeycomb superlattice was obtained (Figure 2b). The formation of quasi-honeycomb structure results from the occupation of nanoparticles at the second layer onto the 3-fold hollow sites of the first layer, as shown in Figure 2c. This conformation was confirmed by the tilt technique ($\pm 15^\circ$) in TEM observation (Supporting Information, Figure S2). The formation of a similar quasi-honeycomb structure was reported for CoPt₃ nanoparticles.⁸ This fact surprised us because, in general, small metal nanoparticles are mainly placed on 2-fold saddle sites of the first layer of superlattices. Actually, in the bilayer system of TBA-Au nanoparticles, the second layer tends to occupy 2-fold saddle sites to form line or circle structures. A similar tendency has been observed in superlattices of larger metal nanoparticles, such as 3–5-nm tetra-*n*-octylammonium bromide-protected Au nanoparticles² and 4.5-nm dodecanethiol-protected silver nanoparticles.⁴ For much larger nanoparticles with large numbers of protective ligands, such as 5.5-nm dodecanethiol-protected Au nanoparticles, 3-fold hollow sites of the first layer of the hcp superlattice start to be occupied.⁵ The formation of the quasi-honeycomb superlattice might be also due to strong hydrogen bonds between BTCA molecules. When 2,6-naphthalenedicarboxylic acid was also used in a similar fashion as an organic acid, well-ordered hcp superlattices were obtained but quasi-honeycomb structures were hardly observed, strongly indicating the contribution of interligand multi-hydrogen bonds to the formation of quasi-honeycomb structures. A planar honeycomb structure would be obtained by reverse deionization of the ammonium salts from this quasi-honeycomb structure, since deionization leads to the formation of naked TBA-Au nanoparticles without organic acids, followed by dropping the second layer particles to the first layer.

While TBA-BTCA-Au nanoparticles have a strong tendency to form hcp superlattices, well-ordered hcp superlattices were hardly formed for TBA-AcOH-protected Au (TBA-AcOH-Au) nanoparticles (Figure 3a). It is quite noteworthy that the 4-fold symmetric square superlattice was often observed on the grid (Figure 3b). In this system, a lack of hydrogen bonds between organic acids and weak Coulomb repulsion between the particles may affect the resulting superlattice structure, but the details are unclear at present and under investigation.

In the present work, a novel method was developed for the fabrication of 2D superlattices. Same-surface amino-functionalized Au nanoparticles as building blocks were self-assembled to form

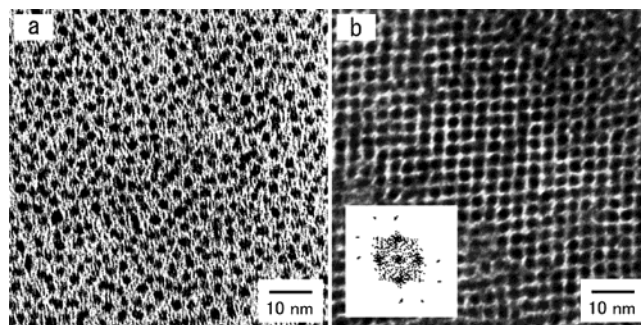


Figure 3. TEM image of TBA-AcOH-Au nanoparticles. (a) Typical amorphous structure and (b) square structure. The inset in (b) shows a FFT image.

different symmetric 2D superlattices using some organic acids. The 2D superlattices of quasi-honeycomb and square structures were obtained by neutralizing amino-functionalized Au nanoparticles with 1,3,5-tribenzenecarboxylic acid and acetic acid, respectively. The results strongly suggest that different types of 2D or 3D superlattices can be constructed by the simple addition of the proper acid to nanoparticles functionalized with amino groups. This method will allow us to obtain various desired metal superlattices without fully synthesizing the ligands.

Acknowledgment. The present work was supported by PRESTO, Japan Science and Technology Corporation (T.T.), and by a Grant-in-Aid for Young Scientists (A) (No. 15681009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (T.T.).

Supporting Information Available: Synthetic procedure and characterization data of TBA, neutralization procedure of TBA-Au, and Figures S1 and S2 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kiely, C. J.; Fink, J.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Nature* **1998**, *396*, 444.
- (2) Fink, J.; Kiely, C. J.; Bethell, D.; Schiffrin, D. J. *Chem. Mater.* **1998**, *10*, 922.
- (3) Teranishi, T.; Haga, M.; Shiozawa, Y.; Miyake, M. *J. Am. Chem. Soc.* **2000**, *122*, 4237.
- (4) Korgel, B. A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. J. *Phys. Chem. B* **1998**, *102*, 8379.
- (5) Lin, X. M.; Jaeger, H. M.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **2001**, *105*, 3353.
- (6) Teranishi, T.; Hasegawa, S.; Shimizu, T.; Miyake, M. *Adv. Mater.* **2001**, *13*, 1699.
- (7) Shimizu, T.; Teranishi, T.; Hasegawa, S.; Miyake, M. *J. Phys. Chem. B* **2003**, *107*, 2719.
- (8) Shevchenko, E. V.; Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 11480.
- (9) Schmid, G.; Baumle, M.; Beyer, N. *Angew. Chem., Int. Ed.* **2000**, *39*, 181.
- (10) Teranishi, T.; Sugawara, A.; Shimizu, T.; Miyake, M. *J. Am. Chem. Soc.* **2002**, *124*, 4210.
- (11) Zheng, J.; Zhu, Z.; Chen, H.; Liu, Z. *Langmuir* **2000**, *16*, 4409.
- (12) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978.
- (13) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R. *Science* **1996**, *272*, 1323.
- (14) Kim, S.-H.; Medeiros-Ribeiro, G.; Ohlberg, D. A. A.; Williams, R. S.; Heath, J. R. *J. Phys. Chem. B* **1999**, *103*, 10341.
- (15) Beverly, K. C.; Sampaio, J. F.; Heath, J. R. *J. Phys. Chem. B* **2002**, *106*, 2131.
- (16) Frankamp, B. L.; Boal, A. K.; Rotello, V. M. *J. Am. Chem. Soc.* **2002**, *124*, 15146.
- (17) Kim, B.; Tripp, S. L.; Wei, A. *J. Am. Chem. Soc.* **2001**, *123*, 7955.
- (18) Pileni, M. P. *Langmuir* **1997**, *13*, 3266.
- (19) Martin, J. E.; Wilcoxon, J. P.; Odinek, J.; Provencio, P. *J. Phys. Chem. B* **2002**, *106*, 971.
- (20) Petroski, J. M.; Green, T. C.; El-Sayed, M. A. *J. Phys. Chem. A* **2001**, *105*, 5542.

JA035187J