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# Self-Organization of Au Nanoparticles Protected by 2,6-Bis(1′-(8-thiooctyl)benzimidazol-2-yl)pyridine

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The fabrication of ordered metal nanoparticles with well-defined 2-dimensions (2D) would enable us to produce novel optical devices and nanoelectronic devices.[1] Especially, monodispersed gold (Au) nanoparticles have attracted attention as promising optical devices, and furthermore they also have the potentiality to be the building blocks for nanoelectronic devices by means of the single-electron tunneling effect.[2] Au nanoparticles smaller than 2 nm in size are required for such devices to make use of the phenomenon of Coulomb blockade at room temperature.[3] To order nanoparticles on a substrate by evaporating the solvent from the nanoparticle dispersion, one has to use a rigid stabilizer such as ligand or surfactant for Au nanoparticles to form 2D nanoparticle monolayer of a complete hexagonal network, because the volume change of stabilizer like linear polymer through the evaporation of the solvent may suppress the complete arrangement of nanoparticles. In fact, 2.6 nm polyacrylonitrile-protected Au nanoparticles prepared previously formed only a partially hexagonal network.[4] Many efforts have been made to fabricate 2D Au nanoparticle monolayer using self-assembly technique,[1a−c,5] electrophoretic deposition,[6] LB technique,[7] electrostatic interaction,[8] and DNA hybridization,[9] but the only research on 2D ordering of Au nanoparticles smaller than 2 nm in the wide range has been recently reported by Schmid et al.[10] They also succeeded in preparing the micrometer sized crystals of 3D close packed $Au_{55}(PPh_3)_{12}Cl_6$ nanoparticles.[11] Here we describe the synthesis of Au nanoparticles smaller than 2 nm with quite narrow size distribution and their 2D self-organized monolayer by using a newly synthesized protective ligand, 2,6-bis(1′-(8-thiooctyl)benzimidazol-2-yl)pyridine. This ligand was designed to have two functional groups, a disulfide group and a 2,6-bis(benzimidazol-2-yl)pyridine (BIP) group, the former serving to produce small Au nanoparticles and the latter inducing the interaction between the ligands. Moreover, BIP group can form a complex with metal ions, such as $Ru^{2+}$, to provide novel electronic and optical materials.[12]

2,6-Bis(1′-(8-thiooctyl)benzimidazol-2-yl)pyridine (TOBIP, see inset in Figure 1) was synthesized as follows: The mixture of 2,6-bis(benzimidazol-2-yl)pyridine (3.2 mmol) and the suspension of NaH (7.0 mmol) in dimethylformamide (DMF, 14 mL) was heated to 80 °C for 2 h under $N_2$. The resulting solution was added to 1,8-dibromooctane (19.2 mmol) in DMF (15 mL) dropwise at room temperature and then heated to 100 °C for 2 h to obtain 2,6-bis(1′-(8-bromooctyl)benzimidazol-2-yl)pyridine. To the solution of this compound (1.5 mmol) in dried THF (10 mL), a solid of thioacetic acid (13 mmol) was added at room temperature, and then the solution was heated at 50 °C for 14 h, resulting in the formation of 2,6-bis(1′-(8-thioacetyloctyl)benzimidazol-2-yl)pyridine, which was purified by column chromatography on silica gel with ethyl acetate/hexane (1:2) as an eluent. The solution of this compound (0.80 mmol) in methanol/ethanol (4:1, v/v) was degassed by bubbling Ar for 5 min. After $K_2CO_3$ (2.0 mmol) was added to the solution and stirred at room temperature for 21 h, the color changed from orange to pearl orange. Thus, the desired compound, TOBIP, was separated from the thiol by column chromatography on a silica gel with ethyl acetate/ether (4:1) as a pale yellow oil. The final product was identified as TOBIP with $^1H$ NMR and electrospray ionization Fourier transform ion cyclotron resonance (ESI FT ICR) MS. The Au nanoparticles were prepared using TOBIP as a protective agent. In a typical preparation, 2.5 mL of 1 mM aqueous solution of $HAuCl_4 \cdot 4H_2O$ was added to the mixture of 1 mL of 2.5 mM DMF solution of TOBIP and 44 mL of DMF. After heating the solution to 60 °C, 2.5 mL of 10 mM aqueous solution of $KBH_4$ was added to the solution, and stirred vigorously for 1 h to obtain TOBIP-protected Au nanoparticles.

The $[AuCl_4]^-$ solution turned from yellow to brownish red, immediately after the addition of $KBH_4$ aqueous solution. In UV−vis spectrum of the resulting solution, the peak at 320 nm assigned to $[AuCl_4]^-$ ions and $\pi-\pi^*$ transition of TOBIP decreased after adding $KBH_4$, and the broad tailing absorption was observed in

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(1) (a) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629. (b) Terrill, R. H.; Postlethwaite, T. A.; Chen, C.; Poon, C.-D.; Terzis, A.; Chen, A.; Hutchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Falvo, M.; Johnson Jr., C. S.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 12537. (c) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690. (d) Alivisatos, A. P. *Science* **1996**, *271*, 933. (e) Xia, Y.; Kim, E.; Mrksich, M.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 601. (f) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60. (g) Hahn, R. E.; Seraphin, B. O. In *Physics of Thin Film*; Academic: New York, 1978. (h) Kastner, M. A. *Phys. Today* **1993**, 24.

(2) (a) Averin, D. V.; Likaharev, K. K. *J. Low Temp. Phys.* **1986**, *62*, 345. (b) Feldheim, D. L.; Grabar, K. C.; Natan, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 7640.

(3) (a) Bigioni, T. P.; Harrell, L. E.; Cullen, W. G.; Guthrie, D. E.; Whetten, R. L.; First, P. N. *Eur. Phys. J. D* **1999**, *6*, 355. (b) Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 12384. (c) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101. (d) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 202. (e) 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. (f) Janes, D. B.; Kolagunta V. R.; Osifchin, R. G.; Bielefeld, J. D.; Andres R. P.; Henderson J. I.; Kubiak C. P. *Superlattices Microstruct.* **1995**, *18*, 275. (g) Feldheim, D. L.; Grabar, K. C.; Natan, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 7640.

(4) (a) Teranishi, T.; Kiyokawa, I.; Miyake, M. *Adv. Mater.* **1998**, *10*, 596. (b) Teranishi, T.; Kiyokawa, I.; Tanaka, T.; Miyake, M., unpublished result.

(5) (a) Kiely, C. J.; Fink, J.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Nature* **1998**, *396*, 444. (b) Harfenist, S. A.; Wang, Z. L.; Alvarez, M. M.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem.* **1996**, *100*, 13904. (c) Wang, Z. L. *Adv. Mater.* **1998**, *10*, 13. (d) Sarathy, K. V.; Kulkarni, G. U.; Rao, C. N. R. *Chem. Commun.* **1997**, 537. (e) Sarathy, K. V.; Raina, G.; Yadav. R. T.; Kulkarni, G. U.; Rao, C. N. *J. Phys. Chem. B* **1997**, *101*, 9876. (f) Fink, J.; Kiely, C. J.; Bethell, D.; Schiffrin, D. J. *Chem. Mater.* **1998**, *10*, 922. (g) Connolly, S.; Fullam, S.; Korgel, B.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1998**, *120*, 2969.

(6) (a) Giersig, M.; Mulvaney, P. *J. Phys. Chem.* **1993**, *97*, 6334. (b) Giersig, M.; Mulvaney, P. *Langmuir* **1993**, *9*, 3408.

(7) (a) Heath, J. R.; Knobler, C. M.; Leff, D. V. *J. Phys. Chem.* **1997**, *101*, 189. (b) Mayya, K. S.; Patil, V.; Sastry, M. *Langmuir* **1997**, *13*, 2575.

(8) (a) Peschel, S.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1442. (b) Zhu, T.; Fu, X. Y.; Mu, T.; Wang, J.; Liu, Z. F. *Langmuir* **1999**, *15*, 5197. (c) Schmitt, J.; Machtle, P.; Eck, D.; Mohwald, H.; Helm, C. A. *Langmuir* **1999**, *15*, 3256. (d) Mayya, K. S.; Sastry, M. *Langmuir* **1999**, *15*, 1902. (e) Yonezawa, T.; Onoue, S.; Kunitake, T. *Chem. Lett.* **1999**, *10*, 1061.

(9) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.

(10) Schmid, G.; Bäumle, M.; Beyer, N. *Angew. Chem., Int. Ed.* **2000**, *39*, 181.

(11) Schmid, G.; Pugin, R.; Sawitowski, T.; Simon, U.; Marler, B. *Chem. Commun.* **1999**, 1303.

(12) (a) Xiaoming, X.; Haga, M.; Matsumura-Inoue, T.; Ru, Y.; Addison, A. W.; Kano, K. *J. Chem. Soc., Dalton Trans.* **1993**, 2477. (b) Haga, M.; Kato, N.; Monjushiro, H.; Wang, K.; Hossain, M. D. *Supramol. Sci.* **1998**, *5*, 337. (c) Haga, M.; Wang, K.; Kato, N.; Monjushiro, H. *Mol. Crys. Liq. Crys.* **1999**, *337*, 209.

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**Table 1.** Influence of the Amount of TOBIP Ligand on the Mean Diameters and Standard Deviations of Au Nanoparticles

| sample no. | TOBIP/Au (mol/mol) | mean diamter (nm) | standard deviation (nm) |
|---|---|---|---|
| 1 | 0.05 | 3.2 | 0.76 |
| 2 | 0.1 | 2.7 | 0.51 |
| 3 | 0.5 | 2.3 | 0.40 |
| 4 | 1.0 | 1.9 | 0.39 |

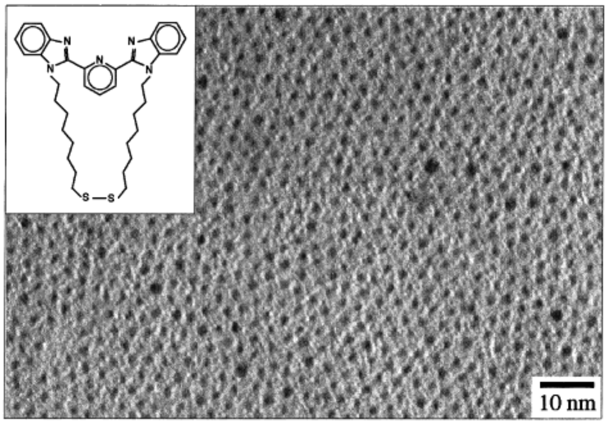

**Figure 1.** TEM image of TOBIP-protected Au nanoparticles (TOBIP/Au = 1/1 (mol/mol)). The inset stands for the chemical structure of TOBIP ligand.

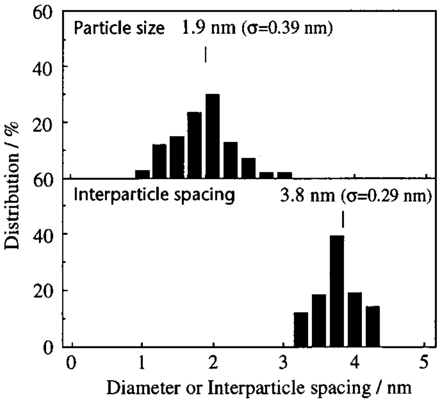

**Figure 2.** Interparticle spacing distribution of 2D self-organized monolayer of TOBIP-protected Au nanoparticles in Figure 1.

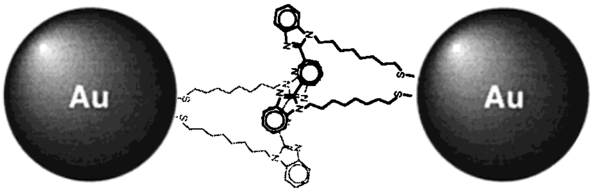

**Figure 3.** Schematic illustration of the interpenetration of TOBIP ligands protecting Au nanoparticles.

the range from the ultraviolet to visible regions due to the formation of the band structure, indicating the formation of Au nanoparticles. Little plasmon resonance at ~520 nm is observed, which means the formation of very small Au nanoparticles.[13] These Au nanoparticles are stably dispersed for at least one year in DMF/$H_2O$ mixed solution under air. Table 1 presents the mean diameters and standard deviations of Au nanoparticles prepared at the TOBIP/Au molar ratios from 0.05 to 1.0. As Leff et al. pointed out, the amount of the protective agent greatly influences the particle size and the dispersity of Au nanoparticles.[14] The mean diameter and standard deviation decreased with an increase in the amount of the protective agent, TOBIP, which was also observed in the preparation of polymer-protected Pd,[15] Pt,[16] and Au nanoparticles.[4] Especially, at TOBIP/Au = 1.0, the monodispersed Au nanoparticles smaller than 2.0 nm were obtained, which are expected to be applied for nanoelectronic devices. The number of TOBIP ligands bound to Au nanoparticle is under investigation. Figure 1 shows the TEM image of TOBIP-protected Au nanoparticles prepared at TOBIP/Au = 1.0. Almost complete hexagonal monolayer of these particles covers the area of ~0.1 $\mu m^2$, and the organization area is extended by increasing the number of drops of Au nanoparticle dispersion on the carbon-coated copper grid. Fourier transform spots are seen with spacings corresponding to the separations of the superlattice planes seen in the monolayer in Figure 1, supporting the long-range ordering in the 2D monolayer.[6b] However, the Au nanoparticles form not a perfect lattice but a mosaic spread in orientation, which might be caused by the lattice defect due to larger particles. Both the size distribution and the interparticle-spacing distribution estimated from Figure 1 are presented in Figure 2. The mean interparticle spacing is estimated to be ~3.8 nm, meaning the thickness of TOBIP layers between the Au nanoparticles is 1.9 nm. By taking the length of TOBIP molecule to be ~1.5 nm into consideration, this result suggests that each Au nanoparticle is stabilized by one TOBIP layer, and presumably the TOBIP ligands are interpenetrating each other as a result of a $\pi-\pi$ interaction of BIP groups, as shown in Figure 3. This $\pi-\pi$ interaction may contribute to the self-organization of Au nanoparticles. The high DMF concentration in solution has strongly influenced the long-range order to the resulting structure. The details of the $\pi-\pi$ interaction between the neighboring ligands and the solvent effect are under investigation and will be dealt with in a different paper.[17] The decrease in size dispersity or the size selection of the particles will enable us to obtain the 2D films of complete spatial configuration.

In conclusion, we have successfully prepared 1.9 nm Au nanoparticles protected by TOBIP in DMF/$H_2O$ mixed solvent. The Au nanoparticles generated have quite narrow size distribution and remain stably dispersed for more than one year. Au nanoparticles smaller than 2.0 nm could be obtained by using triphenylphosphine[18] or thiol-derivatives such as a series of alkanethiols,[14] although the formation of their completely hexagonal network has been a difficult problem. Our self-organized Au nanoparticle monolayer covers the area of ~0.1 $\mu m^2$ on the carbon-coated copper grid, presumably due to a $\pi-\pi$ interaction of the TOBIP layer with an adjacent one. This Au nanoparticle monolayer will be applicable for not only optical devices but also novel electronic devices. Syntheses of a series of the ligands with various alkyl chain lengths and preparation of Au nanoparticles by using these ligands are in progress to control the interparticle spacing of 2D self-organized monolayers.

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(13) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706.

(14) Leff. D. V.; Ohara P. C. Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036.

(15) Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594.

(16) (a) Teranishi, T.; Hosoe, M.; Tanaka, T.; Miyake, M. *J. Phys. Chem. B* **1999**, *103*, 3818. (b) Teranishi, T.; Hosoe, M.; Miyake, M. *Adv. Mater.* **1997**, *9*, 65.

(17) Teranishi, T.; Haga, M.; Shiozawa, Y.; Yasuda, E.; Miyake, M. Manuscript in preparation.

(18) Schmid, G. *Inorg. Synth.* **1990**, *7*, 214.