Formation of Nanoparticle Arrays at the Interlayer of Aqueous Phosphate Bilayers

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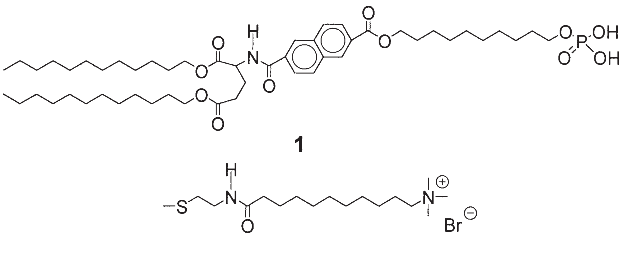
Nanoparticle arrays were obtained by simply mixing anionic bilayer membranes and cationic, quaternary ammonium-stabilized gold nanoparticles under ultrasonication. The particles were immobilized densely into the hydrophilic interlayers of the dispersed lamellar structures and formed quasi one-dimensional structure.

Nanoparticles have been intensively investigated as one of the key materials of recent nanotechnology and catalysis.[1] Especially, preparation of low-dimensional arrays of metal and semiconductor nanoparticles has been a topic of gathering much interest.[2] Two-dimensional arrays on a flat substrate were already reported by simply casting nanoparticle dispersions.[3] On the other hand, preparation of one-dimensional arrays is more difficult due to the lack of proper templates. Recently, Murakoshi, et al. reported one-dimensional array of gold nanoparticles on Au(111) surface by light-irradiation.[4] However, to keep the array structure stably, strong interactions between templates and particles are needed. Mann et al. reported formation of nanoparticle arrays by reducing $AuCl_4^-$ in the presence of bilayer, but densely packed nanoparticles were not obtained.[5]

Electrostatic interactions are the most frequently used interaction to form ordered nanoparticle arrays. However, in many cases, the particles could not be densely packed on the templates, owing to the electrostatic repulsion operating between them. We have recently reported that the repulsive forces can be overwhelmed by the use of highly charged solid surfaces, on which nanoparticles were densely accumulated by electrostatic interaction.[6] Cationic gold nanoparticles were also shown to form wide one-dimensional arrays when they bind to DNA molecules.[7] In this study, we report formation of nanoparticles-bilayer supramolecular assemblies in which nanoparticles are intercalated at the interlayer of aqueous phosphate bilayer structure as quasi one-dimensional arrays.

The anionic bilayer template employed here was formed by $2C_{12}$-L-Glu-Naph$C_{10}PO_4H_2$ (**1**).[8] The amphiphile **1** possesses a phosphate head group, which forms hydrogen-bond-networks at the anionic bilayer surface,[9] and provides intact bilayer structures upon the binding of cationic nanoparticles. In addition, naphthalene rings give additional stability to the bilayer by the stacking interactions. As the stabilizing reagent of cationic nanoparticles, ω-mercaptoalkyltrimethylammonium bromide (**2**) was used. Cationic gold nanoparticles were prepared by modifying Brust's method.[6,10] The obtained particles were quite stable and no aggregates were found for months. Excess stabilizers were removed out by re-precipitation of nanoparticles. The nanoparticles were kept in powder form and re-dispersed into water before mixing with the dispersion of **1**. Their average diameter and its standard deviation were 2.2 nm and 0.6 nm, respectively. TEM images were taken with JEOL 200-CX (HVEM Lab., Kyushu Univ.) at the acceleration voltage of 200 kV.



Scheme 1.

Figure 1 shows the TEM image of the bilayer structure formed by **1**. **1** was injected into Tris Buffer (pH = 7.5, $[\mathbf{1}] = 5.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) and the mixture was sonicated for several minutes to form bilayer structures. The sample was stained by phophotungstic acid. A drop was put on a carbon-coated TEM grid. As clearly shown in the image, **1** forms multilayered bilayer structure according to the strong inter-molecular interactions. In the inter-bilayer, the negatively charged hydrophilic groups are aligned, and it provides an ideal space for the accumulation of positively-charged nanoparticles.

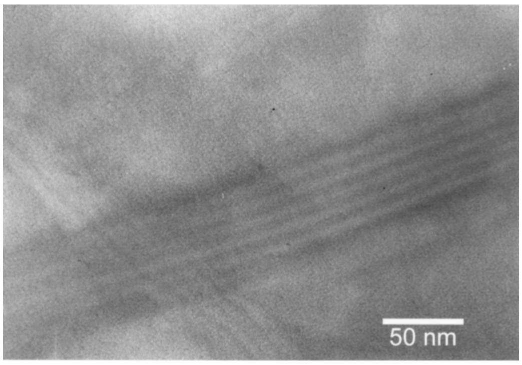


Figure 1. Transmission electron micrograph of the bilayer structure of **1**. Phosphotungstic acid (2.0 wt%) was used as the staining reagent.

The above dispersion of **1** (1 cm^3) and aqueous dispersion of **2**-stabilized gold nanoparticles ($[Au] = 1.8 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, 1 cm^3) were mixed and then the mixture was sonicated for several minutes. The mixed dispersions were highly stable and showed scattering characteristic to the large bilayer structures. In addition, formation of precipitates was not observed. This indicates that the bilayer structure of **1** is intact upon the binding of **2**-stabilized gold nanoparticles. A drop of the mixture was put onto a carbon-coated TEM grid and was observed without

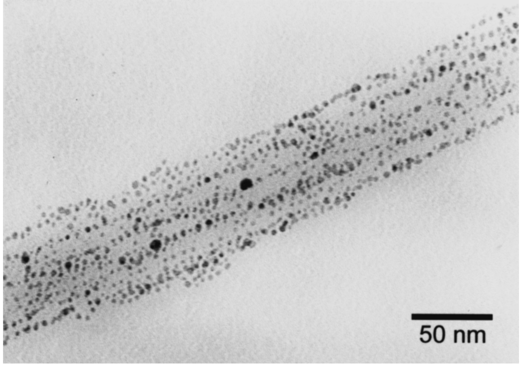


Figure 2. Transmission electron micrograph of the composite of anionic bilayer **1** and **2**-stabilized cationic gold nanoparticles. No staining was conducted.

staining (Figure 2).

By comparing with Figure 1, it appears that the macroscopic structure of the bilayer was not changed by addition of gold nanoparticles. Black dots, indicating cationic gold nanoparticles were aligned almost one-dimensionally between the gray areas densely. The width of the gray area is approximately 10 nm, which corresponds to the twice of the molecular length of **1** (4.7 nm × 2). This indicates that cationic gold nanoparticles are intercalated into the negatively charged hydrophilic interlayer of the bilayer **1** by electrostatic interaction. The gel–liquid crystal transition temperature of **1** is as high as 69 °C,[8] and no structural deformation was generated even after the incorporation of highly positively charged particles. TEM observation was carried out in a wide area on the grid. However, no two-dimensional array of nanoparticles was observed under the employed experimental conditions and mainly quasi one-dimensional arrays in the multilayered interlayers were found. On the other hand, when a drop of bilayer **1** was cast onto a TEM grid and a drop of **2**-stabilized gold nanoparticles was successively put onto the grid, the particles were only adsorbed on the peripheries of the bilayer and were not located in the inter-layer area (data not shown). It is likely that the ultrasonication process is indispensable to form the densely organized nanoparticles. In fact, the layer-by-layer assembly of layer of **1** and **2**-stabilized gold nanoparticles, produces two-dimensionally accumulated cationic nanoparticles on the surface of **1**.[11] When sodium dialkylphosphates $(CH_3(CH_2)_n)_2PO_4Na$ (n = 11, 13, 15) were employed as anionic bilayers and they are mixed with **2**-stabilized gold nanoparticles, precipitates were formed and soluble arrays of nanoparticles were not obtained. Therefore, it is apparent that the chemical structure of phosphate amphiphiles is of crucial importance to obtain the soluble nanoparticles-bilayer supramolecular assemblies in water.

In summary, quasi one-dimensional arrays of cationic metal nanoparticles were formed by the use of rigid bilayer membrane as the template. Thanks to the high rigidity of the bilayer structure, the cationic nanoparticles could be incorporated in the hydrophilic inter-bilayer without deformation of the bilayer structure. The particles were assembled densely, and the complexed superstructure is stably dispersed in water. This assembly formation procedure can be applied to the wide range of charged nanoparticles.

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References and Notes

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1 For example: T. Yonezawa and N. Toshima, *New J. Chem.*, **1998**, 1179; G. Schmid and G. L. Hornyak, *Curr. Opin. Solid State Mater. Sci.*, **2**, 204 (1997); M. T. Reetz, M. Winter, G. Dumpich, J. Lohau, and S. Friedrichowski, *J. Am. Chem. Soc.*, **119**, 4539 (1997); A. P. Alivisatos, *Science*, **271**, 933 (1996); K. Esumi, A. Suzuki, A. Yamahira, and K. Torigoe, *Langmuir*, **16**, 2604 (2000).

2 J. Schmitt, G. Decher, W. J. Dressick, S. L. Brandow, R. E. Geer, R. Shashidhar, and J. M. Calvert, *Adv. Mater.*, **9**, 61 (1997).

3 For example: T. Yonezawa, S. Onoue, and N. Kimizuka, *Langmuir*, **17**, 2291 (2001); B. A. Korgel, S. Fullam, S. Connolly, and D. Fitzmaurice, *J. Phys. Chem. B*, **102**, 8379 (1998); C. J. Kiely, J. Fink, M. Brust, D. Bethell, and D. J. Schiffrin, *Nature*, **396**, 444 (1998).

4 K. Murakoshi and Y. Nakato, *Adv. Mater.*, **12**, 791 (2000).

5 S. L. Burkett and S. Mann, *Chem. Commun.*, **1996**, 321.

6 T. Yonezawa, S. Onoue, and T. Kunitake, *Adv. Mater.*, **10**, 414 (1998); T. Yonezawa, S. Onoue, and T. Kunitake, *Chem. Lett.*, **1999**, 1061.

7 T. Yonezawa, S. Onoue, and T. Kunitake, *Koubunshi Ronbunshu*, **59**, 855 (1999).

8 J.-M. Kim and T. Kunitake, *Memoires Faculty Eng., Kyushu Univ.*, **49**, 93 (1989).

9 N. Kimizuka, A. Baba, and T. Kunitake, *J. Am. Chem. Soc.*, **123**, 1764 (2001).

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

11 T. Yonezawa, S. Onoue, and T. Kunitake, *Stud. Surf. Sci. Catal.*, **132**, 623 (2001).