Metal Coating of DNA Molecules by Cationic, Metastable Gold Nanoparticles

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Metastable cationic gold nanoparticles were newly developed by the use of thiocholine bromide (TCB) as stabilizer. The gold nanoparticles electrostatically bound to DNA molecules and then underwent self-fusion into the wire-like structures. The use of TCB as a labile ligand was essential to achieve non-electrochemical plating of the non-conductive molecules.

Metal coating of organic materials has been widely used to manipulate electronic circuits. Evaporation of metals with masks is one of the most fundamental techniques to produce metal wires or circuits. However, in order to downsize such metal circuits, the ability to produce narrower metal wires is required. Fine lithography, for example, is one promising technique. On the other hand, the development of ''bottom-up'' nanotechnology may replace the conventional ''bulk-down'' approach.[1,2] Metal nanoparticles are attracting much interest as elements for nanocircuits. Assembling metal nanoparticles into low-dimensional arrays or three-dimensional aggregates has been intensively studied due to the expected novel properties which cannot be achieved either from bulk metals or metal complexes.[3,4] Electrostatic interactions have been frequently used to accumulate charged metal nanoparticles on templates.[5–7] However, in many cases, electrostatic repulsion between the particles prevents them from packing at high density.[5] We have previously reported that densely packed monolayers of anionic gold nanoparticles can be formed on the cationic monolayer of synthetic amphiphiles.[6,7] In addition, when cationic gold nanoparticles were adsorbed on DNA molecules or anionic bilayer membranes, low-dimensional arrays of nanoparticles were obtained.[8,9] Sastry recently reported that the lysine-stabilized gold nanoparticles were also electrostatically adsorbed and accumulated on synthetic DNA molecules.[10]

In this study, we describe the formation of wire-like structures templated by λ-DNA molecules from cationic, *metastable* gold nanoparticles. The cationic stabilizer molecule used in this study is thiocholine bromide (TCB: $HS\text{-}(CH_2)_2\text{-}N(CH_3)_3{}^+Br^-$), which was obtained by hydrolysis of commercially available acetylthiocholine bromide (Aldrich). The purity of the product was confirmed by FT-IR, ^{1}H NMR and elemental analysis. The length of the cationic part of TCB($HS\text{-}(CH_2)_2\text{-}N(CH_3)_3$) is ca. 8.1 Å, which is the smallest quaternary ammonium-terminated thiol molecule available. The gold nanoparticles were prepared by $NaBH_4$-reduction of $HAuCl_4$ in the presence of TCB at a Au/TCB ratio of 1 : 3 (mol/mol), similar to Brust's method.[11] The obtained particles could be readily dispersed homogeneously into water even at a high concentration but not in methanol or in other organic solvents.

A transmission electron microscopic (TEM) image and the size distribution of the TCB-stabilized gold nanoparticles are shown in Figure 1. The average size is about 2.7 nm, and the particles are fairly mono-dispersed. This is probably due to the efficient complexation between $AuCl_4{}^-$ and TCB during the preparation. Elemental analysis of the TCB-stabilized gold nanoparticles revealed that each particle contains 14.3 wt% of TCB molecules, which indicates that the gold nanoparticle is surrounded by ca. 100 TCB molecules with an occupied surface area of 22.9 Å^2 per molecule (Figure 1c). This occupied area is slightly larger than that of alkylthiol on Au(111) (ca. 21.5 Å^2)[12] or a longer cationic alkylthiol on gold nanoparticles (21.4 Å^2).[8,13] The lower surface density of TCB can be attributed to the electrostatic repulsion between the TCB molecules on the particle surface.

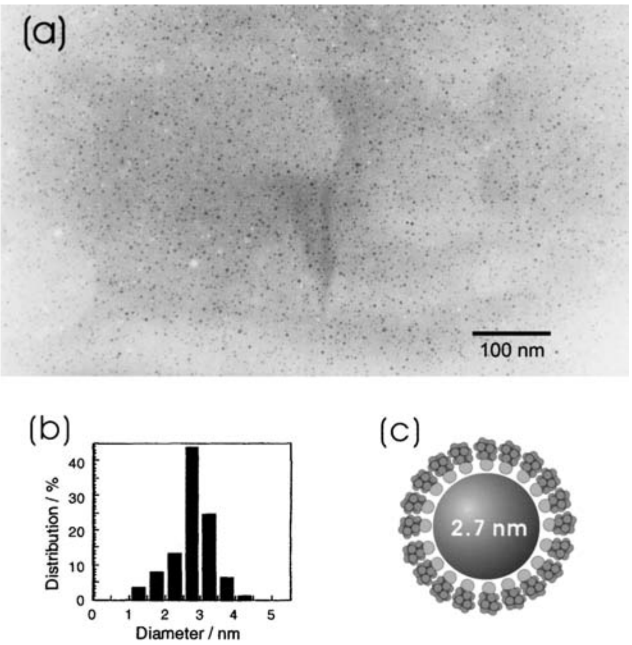

Figure 1. (a) Transmission electron micrograph and (b) the size distribution of thiocholine bromide (TCB)-stabilized gold nanoparticles. (c) Model of TCB-stabilized gold nanoparticle. The image was taken with a Hitachi H-7000 at the acceleration voltage of 100 kV. The size distribution was determined by measuring more than 300 particles in an arbitrarily chosen area in the enlarged TEM image. The model was illustrated by using the elemental analysis data.

The aqueous dispersion of TCB-stabilized gold nanoparticles and λ-DNA in tris buffer (pH $= 7.9$) were mixed with a final concentration of $[Au] = 1.2 \times 10^{-2}$ mol dm^{-3} and $[\lambda\text{-DNA}] = 72\,\mu g\,dm^{-3}$. The mixed solution was immediately sonicated at 0 °C for several seconds in order to obtain homogeneous mixing without decomposition of the DNA molecules. Figure 2 shows the typical TEM images of the gold nanoparticles adsorbed on λ-DNA molecules. These images were taken several hours after sample preparation. Most of the particles were aligned one-

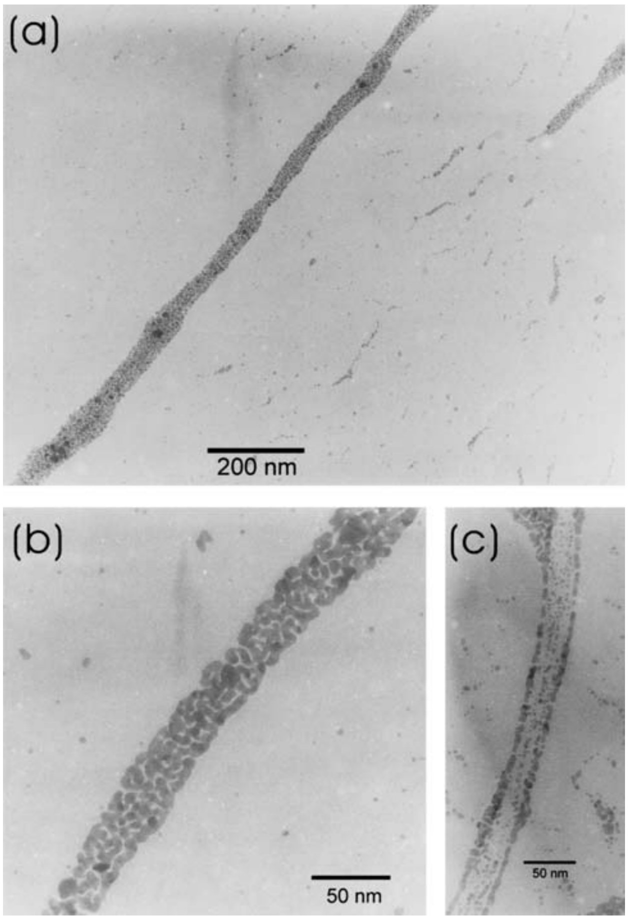

Figure 2. Transmission electron micrographs of TCB-stabilized gold nanoparticles and λ-DNA mixtures. (b) is an enlarged image of (a). Nanoparticles were adsorbed on the side surface of a bundle of DNA molecules (c). The particles grew dramatically compared to those in Fig. 1 and fused with each other to form 1D wire-like structures. The sample was observed the day after the preparation of the mixed dispersion. No obvious transformation of gold nanoparticles was observed under electron beam irradiation at 100 kV.

dimensionally, and the width of the 1D array is ca. 25 nm. These structures are not observed in the absence of DNA, and it is likely that the particles are adsorbed on the bundled DNA molecules. In some cases, nanoparticles were adsorbed preferentially on the edges of the DNA bundles.

Interestingly, by keeping the aqueous mixture at room temperature for several hours, the gold nanoparticles displayed automatic fusion into larger particles in the 1D-assemblies. Fusion of small gold nanoparticles on a TEM grid has been also reported for alkyl-thiol stabilized bimodal nanoparticles with the sizes of 4.5 nm and 7.8 nm, which occurred several months after preparation.[14] The fusion of the particles was explained by the lower stability of the smaller particles, which are truncated cuboctahedra exposing both the {111} and {100} surface facets.[15] It is likely that our 2.7 nm-sized particles are less stable and fuse into the wire-like structure more easily. Haruta et al. indicated that the presence of halogens can promote the growth of gold nanoparticles.[16] In our case, the particles are surrounded by thiocholine bromides, and as the bromide ions would not be totally replaced by the anionic phosphate groups of DNA, they may accelerate the fusion of the particles to form wire-like structures. This is in contrast with our previous reports for the longer quaternary ammonium alkylthiol (length: 2.2 nm)-stabilized gold nanoparticles (particle size: 2.2 nm) that accumulated on DNA molecules or at inter-bilayer spaces without any fusion.[8,9] As TCB contains short ethylene spacer units between the thiol and ammonium groups: $(CH_2)_2$, hydrophobic interaction between them is very weak and this is reflected in the observed larger surface occupied area (22.9 $Å^2$). Consequently, it behaves as a *metastable, labile* ligand compared to the conventional longer alkyl thiols. When these gold nanoparticles are accumulated on DNA, the small inter-particle distances allow them to fuse into the wire-like structure at room temperature.

We have also tried other anionic vinyl polymers such as sodium poly(styrenesulfonate) to produce such nanowires. However in such cases, no 1D array of particles or nanowires was obtained. Instead, aggregated structures were observed, probably for lack of rigidness of the molecules. The present small, highly cationic gold nanoparticles readily bind to DNA, and form the bundles of polyion complexes. The observed linear structure is indicative of the conformational rigidity of the DNA/gold nanoparticle complexes which is absent for the anionic polyelectrolyte/gold nanoparticle complexes.

We have shown the formation of metal nano-wires by DNA-based aqueous nanotechnology. By using a labile short-ammonium bromide thiol as the stabilizing reagent, gold nanoparticles accumulated on DNA molecules display self-fusion at room temperature. Importantly, the fused nanowire-DNA complex remains soluble in the aqueous media. As manipulation and immobilization techniques of DNA molecules have been intensively developed, it should soon be possible to direct the gold nanowires onto the desired positions. We anticipate general application of *metastable* nanoparticles for the non-electrochemical plating of non-conductive materials.

References

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1 W. A. Lopes and H. M. Jaeger, *Nature*, **414**, 735 (2001).

2 L. M. Liz-Marzán and D. J. Norris, *MRS Bull.*, **26**, 981 (2001).

3 C. B. Murray, C. R. Kagan, and M. G. Bawendi, *Annu. Rev. Mater. Res.*, **30**, 545 (2000).

4 M.-P. Pileni, in "Metal Nanoparticles," ed. by D. L. Feldheim and C. A. Foss, Jr., Marcel Dekker, New York (2002), pp 207–236.

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

6 T. Yonezawa, S. Onoue, and T. Kunitake, *Adv. Mater.*, **10**, 414 (1998).

7 T. Yonezawa, S. Onoue, and T. Kunitake, *Chem. Lett.*, **1998**, 689.

8 T. Yonezawa, S. Onoue, and T. Kunitake, *Kobunshi Ronbunshu*, **56**, 855 (1999).

9 T. Yonezawa, S. Onoue, and N. Kimizuka, *Chem. Lett.*, **2002**, 528.

10 A. Kumar, M. Pattarkine, M. Bhadbhade, A. B. Mandale, K. N. Ganesh, S. S. Datar, C. V. Dharmadhikari, and M. Sastry, *Adv. Mater.*, **13**, 341 (2001).

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

12 A. Ulman, *Chem. Rev.*, **96**, 1533 (1996).

13 T. Yonezawa, S. Onoue, and T. Kunitake, *Chem. Lett.*, **1999**, 1061.

14 C. J. Kiely, J. Fink, M. Brust, D. Bethell, and D. J. Schiffrin, *Nature*, **396**, 444 (1998).

15 C. L. Cleveland, U. Landman, M. N. Shafigullin, P. W. Stephens, and R. L. Whetten, *Z. Phys. D: At., Mol. Clusters*, **40**, 503 (1997).

16 M. Haruta, *CATTECH*, **6**, 102 (2002).