# Preparation of Cationic Gold Nanoparticles and Their Monolayer Formation on an Anionic Amphiphile Layer

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Reduction of $AuCl_4^-$ by sodium borohydride in the presence of quaternary ammonium disulfide gave an aqueous dispersion of cationic gold particles in nano-dimension. These cationic nanoparticles could be assembled effectively on an anionic amphiphile layer with a close-packed structure.

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Research on metal nanoparticles has been conducted extensively from expectation to obtain unique and novel functions arising from "quantum size effect".[1] Designed architecture of metal nanoparticles is of great importance for realization of nano-sized devices. For that purpose, formation of one-, two- and three-dimensional regular arrays is indispensable.[2]

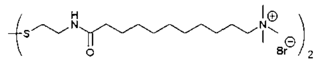
Preparation of close-packed and regularly-ordered monolayers of metal nanoparticles by electrostatic interaction has been described.[3-6] Polyelectrolytes,[4] self-assembled monolayers (SAM),[5] and amphiphile layers[6] have been used to modify underlying substrates for organization of nanoparticles. On the surface of a cationic amphiphile layer, anionic gold and silica nanoparticles were adsorbed effectively thanks to the dense ion sites generated on the surface, giving close-packed monolayers.[6]

The surface of many inorganic materials, such as glass, mica, clay, silver, and metal oxides is negatively charged. These inorganic substrates have been covered with positively charged organic materials to assemble negatively-charged inorganic nanoparticles. In contrast, inorganic nanoparticles themselves have not been functionalized by cationic coordinative stabilizers, probably because stabilized (positively-charged) and un-stabilized (negatively-charged) particles easily form aggregates or precipitates, during the course of surface modification.

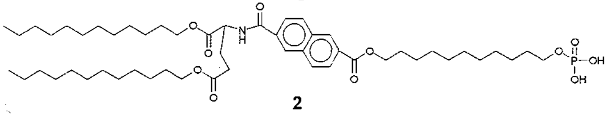
We have prepared cationic gold nanoparticles by direct reduction of $HAuCl_4$ by $NaBH_4$ in the presence of a cationic disulfide stabilizer. The obtained particles are very stable and can be dispersed in water at any pH. Their close-packed monolayer was prepared on the molecular surface of an anionic bilayer amphiphile.

Stabilizing ligand **1** was prepared in the disulfide form: ($\mathbf{1}_2$) (bis(11-trimethylammonioundecanoylaminoethyl)disulfide dibromide) by quaternization of bis(11-bromoundecanoyl-aminoethyl) disulfide[7] with trimethylamine in dry THF. The purity was confirmed by TLC-FID, IR, $^1H$ NMR, and elemental analysis.[8] An aqueous dispersion of cationic gold nanoparticles used here was prepared by reduction of $HAuCl_4$ (30 $cm^3$, $5.0 \times 10^{-3}$ mol $dm^{-3}$) by $NaBH_4$ (5 $cm^3$, $4.0 \times 10^{-1}$ mol $dm^{-3}$) in the presence of $\mathbf{1}_2$ at Au/**1** ratio of 1.0. Amphiphile **2** was synthesized as reported.[9] Other reagents were used as received. Water (> 18 MΩ) was purified by a Mili-Q system.

Many procedures have been proposed for the preparation of gold nanoparticles,[10] including reduction of $AuCl_4^-$ by citrate,[10a-c] borohydride,[10d-f] alcohol,[10g] and light.[10h,i] For our pourpose, reduction by borohydride in the presence of the disulfide stabilizer $(\mathbf{1})_2$, was most suitable. A light-yellow solution of aqueous $AuCl_4^-$ became turbid upon addition of **1**, due to the formation of a salt of $(\mathbf{1})_2$-$2AuCl_4^-$. Immediately after addition of $NaBH_4$ under vigorous stirring, the turbid dispersion turned into dark-red, indicating that reduction was completed. Gold nanoparticles were collected as black powder by addition of acetone to the aqueous dispersion followed by filtration.



$\mathbf{1}_2$



**2**

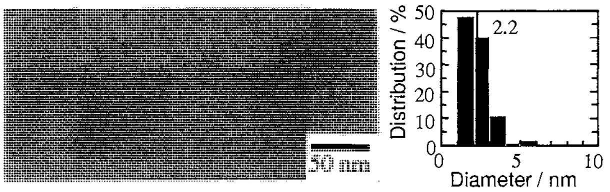


**Figure 1.** Transmission electron microscopic (TEM) image and the size distribution of the 1-stabilized gold nanoparticles. TEM image was taken with JEOL JEM-200 CX (HVEM Lab., Kyushu Univ.) at an acceleration voltage of 200 kV. The sample was prepared by placing a dilute dispersion of gold nanoparticles on carbon coated copper grid and dried. The original magnification: × 100 000.

Figure 1 shows a transmission electron micrograph and the size distribution of **1**-stabilized gold nanoparticles prepared by $NaBH_4$-reduction. The particles have spherical forms and are uniform. The average diameter and its standard deviation are 2.2 and 0.6 nm, respectively. The particles could be kept as powder and were homogeneously re-dispersed in an aqueous media at any concentration.

Excess stabilizers added in the preparation process were removed by repeated (two times) precipitation of the obtained gold nanoparticles by acetone. The precipitates were filtered and washed by acetone several times. Then, the powder was dried under vacuum. Thanks to the strong interaction between Au and S, excess stabilizers alone were removed and the purified gold nanoparticle powder could be re-dispersed readily into water at a wide range of concentrations. Furthermore, these particles could be re-dispersed into water at any pH and even in conc. HCl (35 w%). This result is in sharp contrast with the previous reports that most water-soluble gold nanoparticles stabilized by organic ligands can only be dispersed in alkaline water.[10c,e,f]

Figure 2 shows UV-Vis spectra of the dark-red dispersion of the cationic gold nanoparticles before and after the purification. A surface plasmon band, which is ascribed to a collective oscillation of conduction electrons in response to optical excitation,[11] was found at around 500 nm for the as-prepared sample. The gold nanoparticle was purified by reprecipitation and was re-dispersed in water. The plasmon band of the latter sample was slightly reduced but its peak top (512.5 nm) did not shift. This indicates that size changes due to aggregation or flocculation do not occur during the purification procedure.

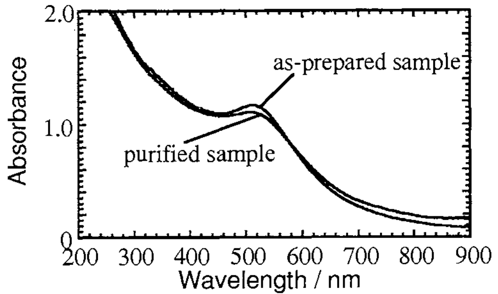


**Figure 2.** UV-Vis spectra of aqueous dispersions of as-prepared and purified **1**-stabilized gold nanoparticles. [Au] = $4.3 \times 10^{-4}$ mol dm$^{-3}$. Jasco V-550 spectrophotometer equipped with a 10-mm quartz cell, 20 °C.

Two-dimensional disposition of the cationic gold nanoparticle was investigated by using anionic bilayer amphiphile **2**. An aqueous dispersion of **2** was deposited on a carbon coated copper grid. After air-drying one day, a drop of the aqueous dispersion of the cationic gold nanoparticle was placed onto the modified grid. Excess dispersion was removed by filter paper. It is reported that synthetic phosphate amphiphiles form multi-bilayer films by casting their dispersions.[9,12] Cationic molecules, such as myoglobin, are intercalated effectively into their anionic sites.[12]

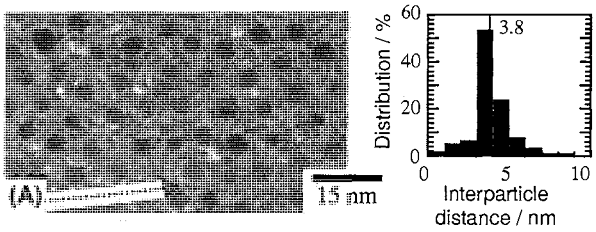


**Figure 3.** TEM image and the distribution of the interparticle distances of the **1**-stabilized gold nanoparticle layer on the surface of the layer of anionic amphiphile **2**. TEM image was taken with a Hitachi H-7500 at an acceleration voltage of 100 kV. The magnification: ×200 000.

Figure 3 shows a TEM image (a) and the distribution of interparticle distance (b) of the deposited gold nanoparticle on the anionic layer of **2**. The specimen was stained by phosphotungstic acid ($P_2O_5 \cdot 24WO_5$, 2 %aq) after the adsorption of the gold nanoparticles. This stain did not change the assembly structure. As can be clearly seen in this image, gold nanoparticles were assembled effectively on the layer of **2** with close-packed structures. At the middle of two particles, gray lines can be observed (A). The trimethylammonium groups of the stabilizing ligand must be bound with the staining agent and be located here. The average inter-particle distance of 3.8 nm is smaller than the two times of the molecular length of **1** (4.4 nm). The stabilizer molecules are apparently not fully extended on the cationic gold nanoparticle.

Directly connecting molecules, such as dithiol compounds[13] or DNA molecules,[14] have been used to assemble colloidal nanoparticles two- or three-dimensionally with close-packed structures against electrostatic repulsion between the particles. No connecting reagent was used in our study. The bilayer of **2** (estimated bilayer thickness: 4.7 nm × 2) cannot act as the connector. We conclude that the gold nanoparticles were assembled by strong electrostatic interaction between densely-located phosphate sites on the layer of amphiphile **2** and the ammonium groups of ligand **1** against the electrostatic repulsion between the cationic particles.

We have demonstrated here that cationic gold nanoparticles are successfully obtained by $NaBH_4$ reduction of $AuCl_4^-$ in the presence of the cationic disulfide stabilizer. The obtained particles were highly stable and could be kept as powder. The powder was highly soluble and could be re-dispersed readily into water without any aggregation even at very low pH. The cationic gold nanoparticles could be assembled effectively with close-packed structure on the anionic amphiphile layer. The implication of this result will be discussed in later publications.

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8 $1_2$; $^1$H NMR ($D_2O$, 250 MHz) δ 1.2-1.7 (m, 32H, $CH_2$), 2.2 (t, 4H, $CH_2CO$), 2.8 (t, 4H, $CH_2S$), 3.1 (s, 18H, $CH_3N^+$), 3.3 (t, 4H, $CH_2N^+$), 3.5 (t, 4H, $CH_2N$). Elemental analysis; Found: C, 49.62; H, 8.86; N, 7.21%. Calcd for $C_{32}H_{68}N_4O_2Br_2S_2$ $1/2H_2O$: C, 49.66; H, 8.98; N, 7.23%.

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