Practical Preparation of Size-Controlled Gold Nanoparticles in Water

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Facile, safe and efficient preparation of stable dispersions of gold nanoparticle from tetrachloroaureic(III) ion is achieved by simultaneous addition of citrate as reductant and sodium 3-mercaptopropionate as stabilizer. No rigorous cleanliness is needed and the reductant is decomposed to CO_2. The particle size can be controlled in the range between 2.3 nm and 10 nm.

Nanoscopic metal colloids and clusters — nanoparticles — have been known for a long time and are now widely investigated as new materials with novel properties.[1, 2] In particular, they are expected as useful functional units in nano-electronic devices based on the quantum size effect. Schmid *et al.* showed that phosphine ligand-stabilized Au_{55} clusters, with a diameter of 1.5 nm, formed an array of quantum dots, and provided tunnel resonance resistors in which the smallest working unit was comprised of pairs of cluster molecules.[3]

It should be interesting to investigate optical properties of copper, gold and silver (group-1B metals) nanoparticles since they strongly absorb light in the visible region due to surface plasmon resonance. Therefore, a large-scale, reliable production of stable, size-controlled nanoparticles of these metals has been strongly desired.

Size reduction of nanoparticles of group-1B metals in water to diameter of 1 or 2 nm is difficult by conventional stabilization with polymers[4, 5] or surfactants.[5] Although it was possible to obtain 1.5-nm gold nanoparticles in water by phosphinium ligands, this preparation required rigorous experimental cleanliness, *i. e.*, washing glass surface with a hydrofluoric acid-containing mixture followed by copious rinsing.[6] Mercapto groups (-SH) have been used as ligands to stabilize gold nanoparticles in recent years. In these cases, however, weak reductants cannot reduce gold ion due to strong bonding of mercapto group and gold ion.[7, 8] Only $NaBH_4$, a stronger, flammable reductant, has been used to reduce mercapto-bonded gold ion.

We describe here a practically advantageous preparative method of gold nanoparticles in water. Sodium 3-mercaptopropionate (MPA-Na, 3-mercaptopropionic acid (Tokyo Kasei Co.), was neutralized with NaOH) and citrate ion were used as stabilizer and reductant, respectively.

Coordination complexes of metal salts and protective reagents were often used to prepare small metal nanoparticles under mild reductive conditions.[4, 5] However, when MPA-Na was injected prior to addition of citrate ion, complete reduction of $[AuCl_4]^-$ could not be achieved because of strong coordination of MPA to$[AuCl_4]^-$. In contrast, mixtures of large particles (diameter : *ca.* 20 nm) and small particles were formed when MPA-Na was injected into the flask after the addition of citrate ion. The small particles are apparently MPA-stabilized gold nanoparticles, while larger ones must be citrate-stabilized particles, since citrate reduction of $HAuCl_4$ gives gold particles of the diameter of *ca.* 20 nm (Figure 2). We improved this procedure by adopting simultaneous addition of stabilizer and reductant: Into refluxing water (250 cm^3) in a 500 cm^3, scratch-free, round-bottom flask, that had been washed with a commercial detergent and water, was added aqueous tetrachloroaureic(III) acid ($HAuCl_4 \cdot 4H_2O$, 5.8×10^{-3} mol dm^{-3}, 25 cm^3) and, the solution was heated to boiling again. Then, the solution (25 cm^3) of MPA-Na and citrate ion (trisodium citrate dihydrate, 2.0 wt%) was injected simultaneously. After the injection of reductant and stabilizer, the color of the solution turned from yellow to red or brown. The larger the stabilizer/gold ratio was, the longer the reduction time became. Thanks to fast, stable complex formation between gold(0) and the mercapto reagent, gold nanoparticles (the total metal concentration: 4.8×10^{-4} mol dm^{-3}) were obtained as stable dispersions. No sign of decomposition or precipitation was seen

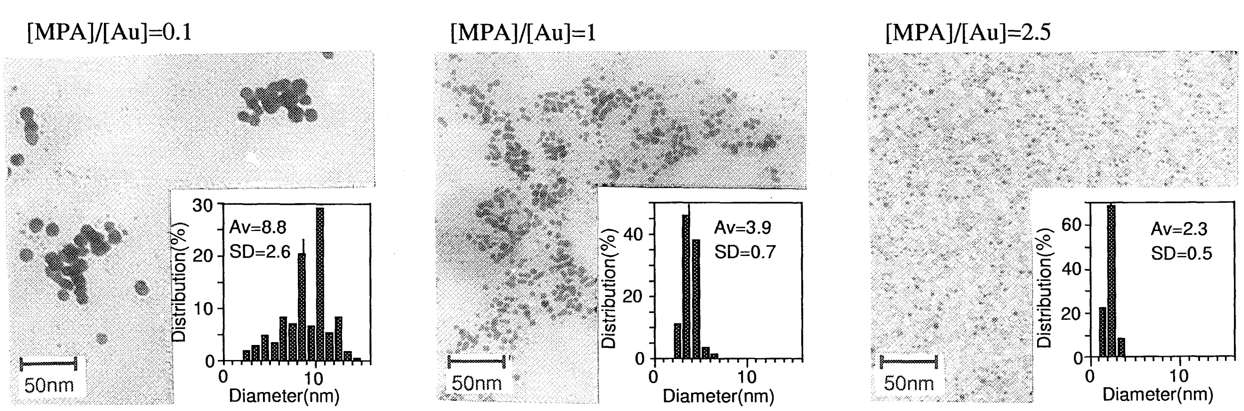

Figure 1. Transmission electron micrographs and size distributions of sodium 3-mercaptopropionate (MPA)-stabilized gold nanoparticles. Size distribution was obtained by measuring diameters of at least 300 particles in an arbitarily chosen area of a TEM photograph.

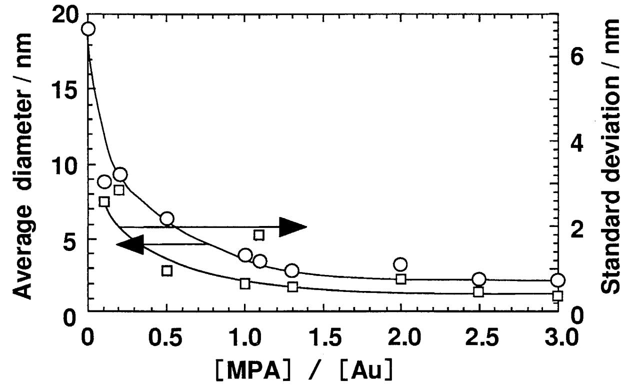

Figure 2. Size variation of gold nanoparticles (○) and their standard deviations (□) with the stabilizer/gold (mol/mol) ratio. Experimental data were obtained from TEM observation.

over a period of several months.

The product was examined using a Hitachi H-600 electron microscope at an acceleration voltage of 75 kV. Some of their TEM photographs and the size distributions obtained are collected in Figure 1. Every gold nanoparticle has a spherical form. Some coagulation was found in TEM photographs with small stabilizer/gold ratios (0.1 - 0.5). The average diameter is affected by the ratio of stabilizer and gold in the range of 2.3 to 10 nm.

Figure 2 gives size variation and its standard deviation in relation to the stabilizer/gold ratio. The standard deviations are rather small, indicating that very efficient coordination of stabilizer to Au(0) atoms or its pre-aggregates prevents formation of larger Au(0) aggregates. Weakly coordinating stabilizers, such as polymers or surfactants, cannot give such small, uniform particles.[4, 5] The size of gold nanoparticles prepared in an organic solvent by $NaBH_4$ reduction in the presence of alkyl thiols is also controlled by the gold/stabilizer ratio,[9] and is rather small compared with that of ours, probably because coordination of the thiol to gold ion preceded the reduction process. However, we could not obtain monodispersed nanoparticles when we applied this method to our MPA-stabilized gold nanoparticles.

UV-Vis spectra of the gold nanoparticle as aqueous dispersions are collected in Figure 3. Gold nanoparticles have a surface plasmon absorption at *ca.* 530 nm.[10] The absorption intensity was enhanced with increasing sizes of gold nanoparticles as predicted theoretically,[11] without large peak shifts.

When the stabilizer/gold ratio is more than 1.5, no typical plasmon absorption was detected at the concentration used, and the color of the dispersions was yellowish brown. This observation is similar to that of Schmid *et al.* for their 1.5 nm gold particles[12] and to that of Brust *et al.* for their 2 nm ones,[7] and is a common feature of the scattering color of small nanoparticles of platinum or palladium which have no plasmon absorption. The particles obtained here appear too small to show plasmon absorption. It is also possible that the strong coordination of S to Au shows a dumping effect on the plasmon absorption.[13]

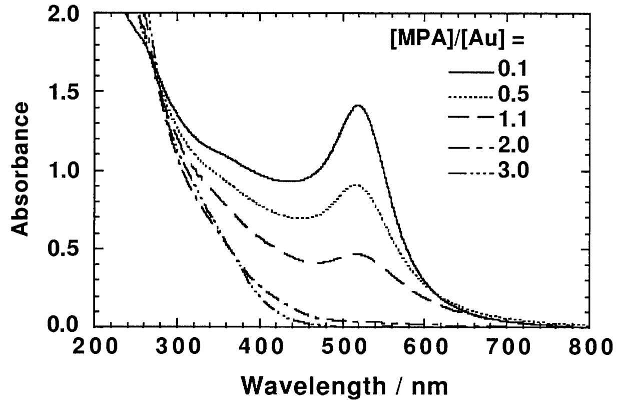

Figure 3. Uv-vis spectra of aqueous dispersions of freshly prepared 3-mercaptopropionate-stabilized gold nanoparticles at various stabilizer/gold ratios. [Au] = 4.8×10^{-4} mol dm^{-3} for all preparations. Samples were measured in a 10 mm quartz cell. The inset numbers show the [stabilizer]/[gold] (mol/mol) ratios.

We have found a simple method to prepare gold nanoparticles with a narrow size distribution by citrate reduction of $[AuCl_4]^-$ in water. This procedure is facile, reproducible, safe and the dispersion thus obtained is very stable. The apparatus needs not be rigorously clean in this procedure. The treatment of the waste should not be costly because the reductant is readily decomposed to CO_2. Further, many functional groups may be introduced onto the particle surface by taking advantages of the carboxylate function of the stabilizer.

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