Cationic Silver Nanoparticles Dispersed in Water Prepared from Insoluble Salts

Tetsu Yonezawa,*[†,††] Hideo Genda,[†] and Kunihito Koumoto[†]
[†]*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Nagoya 464-8603*
[††]*PRESTO "Structure ordering and Physical properties," Japan Science and Technology Corporation, Furo-cho, Nagoya 464-8603*

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Homogeneous and uniform-sized silver nanoparticles were obtained by reduction of insoluble silver halides. As the stabilizing reagent, a small cationic thiol, thiocholine bromide, was used. Even from large crystals of silver halides, nanosized particles were obtained. Under the optimum conditions, highly monodispersed nanoparticles with relative standard deviation of less than 7% were obtained.

During the last decade, there have been many studies on nanomaterials.[1] Especially, nanoparticles having a spherical shape have attracted much interest in the field of chemistry, physics, biology, materials science, and surface science.[2] In almost all cases, homogeneous nanoparticles have been prepared from homogeneous precursor solutions.[1–3] Various soluble metal salts, such as $RhCl_3$, H_2PtCl_6, $HAuCl_4$, have been used as the metal sources of nanoparticles. For example, one of the most commonly referred-to work on the preparation of alkylthiol-stabilized gold nanoparticles by Brust et al. used a phase-transfer reagent to introduce tetrachloroaurate(III) ions ($AuCl_4^-$) into the organic phase homogeneously.[4] Esumi et al. used silver-metal multinuclear complexes as the metal sources of silver-containing bimetallic nanoparticles in order to avoid the formation of insoluble silver halides.[5] It is probably a conventional wisdom that homogeneous colloidal solutions should be prepared from homogeneous precursor solutions. However, even from homogeneous solutions of metal ions, it is relatively difficult to obtain uniform-sized metal nanoparticles with the relative standard deviation of less than 10%.

On the contrary, in the photographic system, which is the most popular application of nanoparticle technology, photoreduction of silver halides to metallic silver nanocrystals is the most important process. In this case, silver halides are ground into fine powder and immobilized in the matrix but uniform silver nanocrystals should be obtained to give fine images with a high resolution.

We have already reported the preparation of homogeneous cationic gold and silver nanoparticles stabilized by a quaternary ammonium bromide terminated thiol with a relatively long alkyl chain.[6,7] The quaternary ammonium bromide group releases bromide anions at any pH and these particles can be dispersed in aqueous media even under acidic conditions. These particles can be assembled densely on DNA molecules or amphiphiles either by a layer-by-layer technique or by mixing.[8] In these cases, stable and homogeneous silver nanoparticles were prepared by $NaBH_4$-reduction of $AgNO_3$ in the presence of a stabilizer.[7] However, AgBr is generated during the reduction as the stabilizer contains bromide ions.

In this study, we chose insoluble silver halides as the metal sources of silver nanoparticles. As the stabilizing reagent, the smallest cationic thiol ligand: thiocholine bromide ($HS–(CH_2)_2–N(CH_3)_3Br$: TCB) was used. Under the optimum conditions, highly homogeneous nanoparticle dispersion was obtained. A smaller stabilizer may be favourable to use the specific properties of nanosize metal core.

TCB was synthesized by hydrolysis of acetylthiocholine bromide (ATCB, Aldrich).[9] The purity was confirmed by FT-IR, ^1H NMR, and elemental analysis.[9a] Water was purified by the Direct-Q system (Millipore, $>18\,M\Omega$).

The process of preparing TCB-stabilized silver nanoparticles is a simple one-pot process similar to Brust's method.[1f,4] In a 100-cm^3 round bottom flask, methanol solution of TCB (6.0×10^{-6} mole, $30\,cm^3$) was introduced. Then, a silver halide (AgCl or AgBr) without pre-treatment was introduced (1.5×10^{-6} mole) into the flask. Aqueous solution of $NaBH_4$ ($4.0 \times 10^{-1}\,mol\,dm^{-3}$, $5\,cm^3$) was then introduced drop by drop under vigorous stirring. The obtained nanoparticles could be purified by the re-precipitation and dispersion method.

AgCl and AgBr are colorless crystals. These crystals did not dissolve into methanol and always remained in crystal form at the bottom of the flask. Under vigorous stirring, a designated amount of aqueous solution of $NaBH_4$ was dropwise introduced into this heterogeneous dispersion. The color of the dispersion became brownish yellow. In the case of the preparation of gold nanoparticles from homogeneous solutions of $AuCl_4^-$, the color of the dispersion was immediately changed by the addition of $NaBH_4$. The rate of this color change to brownish yellow was not so rapid, taking several tens of seconds. Silver nanoparticles often show yellow color, which can be ascribed to the characteristic plasmon absorption of nanosized 0-valent silver crystals. After three hours of stirring, no insoluble products were observed, but slight amounts of black precipitates were sometimes obtained. However, when these methanol dispersions were kept for a long time, brown precipitates formed. These brown precipitates could be readily dispersed into water and gave homogeneous and transparent yellow dispersions. This phenomenon clearly indicates that the injected silver halides were completely reduced and the particle surface was completely covered by TCB molecules.

Figure 1 shows the X-ray diffractograms of TCB-stabilized silver nanoparticles thus obtained from the silver halides. The samples were obtained by re-precipitation from the methanol dispersions by the addition of acetone and were collected by filtration over membrane filters. They were measured directly with the membrane filter and the peak at $2\theta =$ ca. 18° was attributed to the filter. In comparison with JSPDS data, no silver halides (AgCl or AgBr) but only metallic silver nanocrystals could be observed (Figure 1) in both diffractograms. The color of the obtained dispersion and this XRD strongly indicated that the reduction was completed with this process and that this process can provide homogeneous dispersion of cationic silver nanoparticles consisting of only metallic silver atoms (Ag(0)) without the formation of silver halide nanoparticles.

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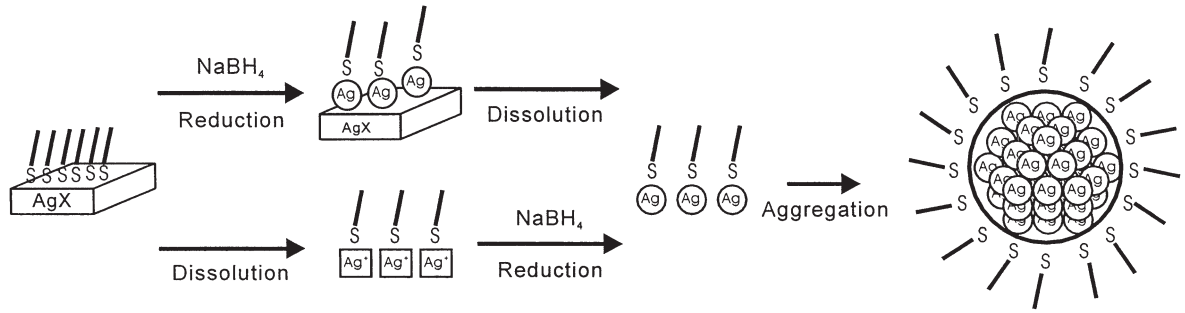

Figure 3. Schematic illustration of formation mechanism of uniform-sized silver nanoparticles from insoluble silver halides.

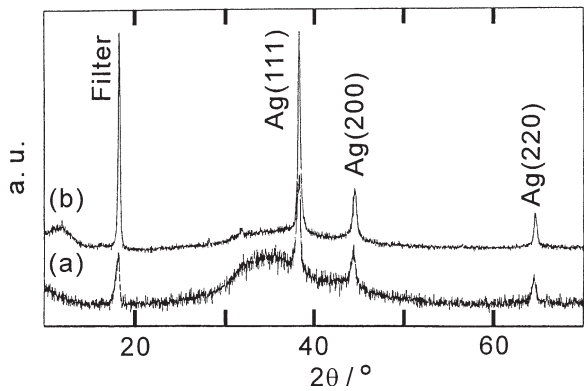

Figure 1. XRD spectrum of TCB-stabilized Ag nanoparticles prepared from (a) AgCl or (b) AgBr at Ag/TCB = 1:3 (mol/mol). Peak at ca. 18° is attributed to the membrane filter paper. Target: Cu Kα.

Figure 2 shows the transmission electron micrograph and the size distributions of the TCB-stabilized silver nanoparticles prepared in methanol from AgCl at Ag:TCB = 1:4 (mol/mol). The obtained particles were also re-precipitated from the methanol dispersion by the addition of acetone. The obtained powder could be readily re-dispersed homogeneously into water without any precipitation. Highly uniform and spherical particles were observed. Some aggregated structures were observed in the image but these were often generated during the evaporation of the aqueous medium on the TEM grid.[10] These particles show a very high monodispersity and the distribution of size closely matches the normal distribution. This is the optimum condition to obtain high monodispersity among the many conditions examined. The average diameter of these particles was 5.9 nm, and the relative standard deviation was as small as 6.8%. The particles prepared with a smaller concentration of TCB, some very large particles were produced.

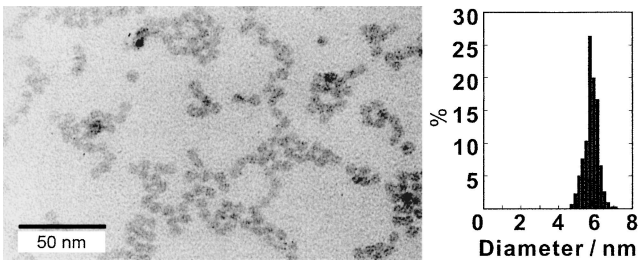

Figure 2. Transmission electron micrograph and particle size distribution of TCB-stabilized Ag nanoparticles prepared at Ag/TCB = 1:4 (mol/mol). Sample was prepared by putting of a drop of the aqueous dispersion of Ag nanoparticles onto carbon-coated Cu grid. The image was taken with a Hitachi H-800 with the acceleration voltage of 200 kV. Size distribution was obtained by the measurement of 300 particles in an arbitrarily chosen area in an enlarged TEM image.

A possible formation route of TCB-stabilized Ag nanoparticles (Figure 3) is proposed. The reduction of Ag^+ is proceeded on the surface of silver halide crystals. In fact, in some cases, the surface of silver halide crystals turned black, indicating that the reduction of Ag^+ to Ag(0) occurred on the surface of the insoluble crystals. 0-valent Ag atoms were dissolved into water and aggregated to form silver nanoparticles. Ag^+-TCB complexes should also be produced and they should be reduced in the disperse medium by $NaBH_4$.

In this paper, we reported on the preparation of homogeneous dispersions of cationic silver nanoparticles by $NaBH_4$-reduction of insoluble silver halides. Even the metal sources did not dissolve into the solution of stabilizer molecules, a homogeneous dispersion of uniform-sized nanoparticles consisting of 0-valent silver atoms was obtained. Under the optimum conditions, the relative standard deviation was as small as ca. 7%.

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