Esterification of Surface Modified Silver Nanoparticles with *n*-Butanol

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Surface modified nanometer-sized silver particles with mercaptosuccinic acid (MSA) are crystallized in the size range of few micron-meter. The esterification of carboxylic acid of MSA on the surface of particles is performed with *n*-butanol, enabling phase transfer from water to organic phase. The yield of esterification was found to be more than 90%.

The synthesis of nanometer-sized particles with well-defined surfaces is a current interest from materials science. Following the first modification on CdSe quantum dot,[1] there are many reports on the formation of self-assembled modification of gold nanoparticles.[2–4] Later, it was applied to silver[5–8] and cobalt.[9] In these studies, the solvents to suspend the nanoparticles are all organic liquids owing to the limitation of modifiers. Recently we have developed a synthetic route for water-soluble nanoparticles.[10] Phase transfer of nanometer-sized particles from water to organic solvent or vice versa is also a current interest, because of wide technological applications. In the previous report, we have demonstrated that gold nanoparticles are transferred from water to hexane through the surface modification with anion-cation interaction.[11] As for the silver particles, it was shown that Ag particles can be transferred through the adsorption by oleic acid.[12] Here we describe a phase transfer from water to butanol using esterification reaction on the surface of silver nanoparticles.

The basic preparation procedure is from Ref. 10. Briefly, 0.5 mmol of $AgNO_3$ aqueous solution (5 w/v% preparation in advance) was first mixed with 1.0 mmol of MSA in 100 mL methanol to give a transparent solution. A freshly prepared 0.2 M aqueous sodium borohydride solution 25 mL was then added through a syringe under vigorous stirring. The color of the solution changed dark-brown immediately and then resulted in a flocculent dark-brown precipitate. After further stirring for 1.5 hr, the sample precipitate was gathered by decantation and centrifugation followed by washing with 20% methanol/water solution. These processes were repeated twice and then washed with ethanol. No dialysis was engaged. The mean diameter of the particles, determined by a transmission electron microscope (TEM), was 4.9 nm with FWHM of 2 nm (Figure 1a). Structure assignment and size estimation were conducted using X-ray diffraction (XRD). XRD patterns of Ag samples can be indexed to that of fcc, indicating the formation of pure silver metallic particles. The average particle size estimated from the Scherrer's equation, according to the half-width of (111) peak corrected with that of bulk Ag, was estimated to be ca. 3.5 nm. This starting material for the surface esterification was abbreviated with Ag-MSA. In order to check the purity of the starting samples in surface modification, crystallization of this particle was conducted. The crystallization (3D super lattice formation) took place 4–10 days in acidic conditions. Figure 2 shows numerous μm size crystallites with clear crystal habit (majority rectangular fringe). Irrespective of the rather wide size distribution, we can get crystallites of nanoparticles. No fractionation process was needed for this crystallization showing that the starting particles are uniformly modified.

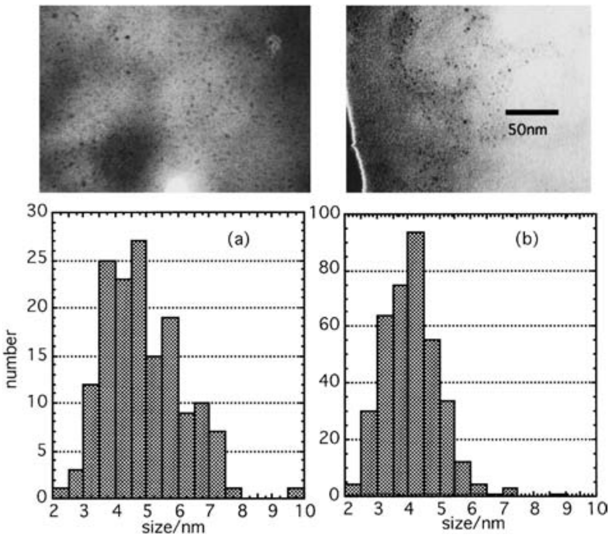

Figure 1. TEM photographs and the size histograms of Ag nanoparticles a) before (Ag-MSA) and b) after (Ag-MSA-Bu) modification by butyl alcohol. Scale bar is the same for both.

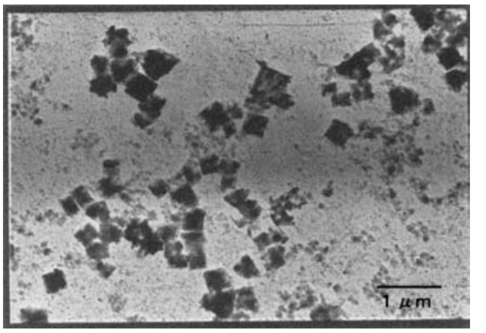

Figure 2. An SEM photograph of 3D particle crystals with MSA modified surface. Numerous rectangular-shaped crystallites are mixed with amorphous deposits from suspension.

Five mL *n*-butanol with 0.1 mL of conc. sulfuric acid was added to 3 mg Ag-MSA powder described above and heated less than 70 °C for 20 min. The color of the suspension changed to brown. Dialysis vz. ethanol was applied in order to remove residual sulfuric acid until the conductivity of the effluent indicated zero. This particle was named as Ag-MSA-Bu. The optical absorption spectra in the visible region (Figure 3) were taken in water (Ag-MSA) and in butanol (Ag-MSA-Bu). Slight red-shift was observed for Ag-MSA-Bu. The size distribution is shown in Figure 1b. The average size was found to be 4.1 nm. A TEM study revealed that the silver particles smaller than 3 nm are

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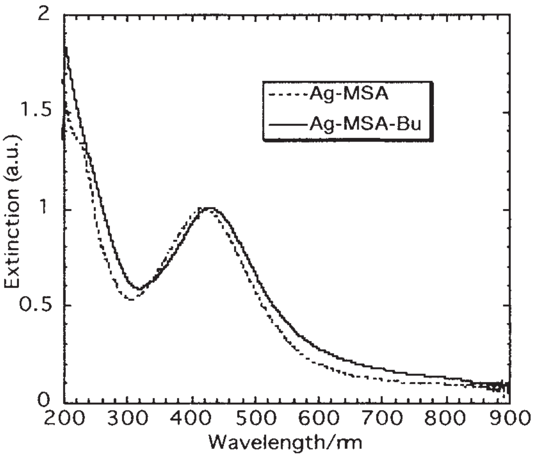

Figure 3. Visible absorption spectra before (Ag-MSA) and after (Ag-MSA-Bu) esterification.

very unstable under electron beam irradiation of normal intensity. Therefore special care should be taken to use extensively dried sample in vacuo and to keep the electron beam as weak as possible during observation.

The surface structure of Ag particles before and after esterification was examined by IR spectra (Figure 4). The formal surface species after esterification are also shown in the inset of Figure 4. The existence of two strong peaks at 1579 $\mathrm{cm^{-1}}$ and 1404 $\mathrm{cm^{-1}}$ in Ag-MSA, which can be attributed to the asymmetric and symmetric stretching vibration of carboxylate ions, respectively, indicates that MSA exists in the form of carboxylate anions before modification.[10b] From elemental analysis, the counter cations were found to be sodium ion.[10a] The absence of S–H vibration peak at 2548 $\mathrm{cm^{-1}}$ of pure MSA gives evidence that MSA combines with silver through sulfur atoms in thiol group. After modification, the carbonyl peak at 1716 $\mathrm{cm^{-1}}$ and ether peak at 1149 $\mathrm{cm^{-1}}$ appeared.[13] Small hump at 2922 $\mathrm{cm^{-1}}$ is from C–H stretching of butyl group. All these findings support that surface carboxylate changed to ester. We have also found that very weak peaks existed at the position of carboxylate ions in this sample, indicating that not all carboxylic acid were converted to ester. A strong O–H band at around 3400 $\mathrm{cm^{-1}}$ in both samples revealed the presence of bound water on the particle surface.

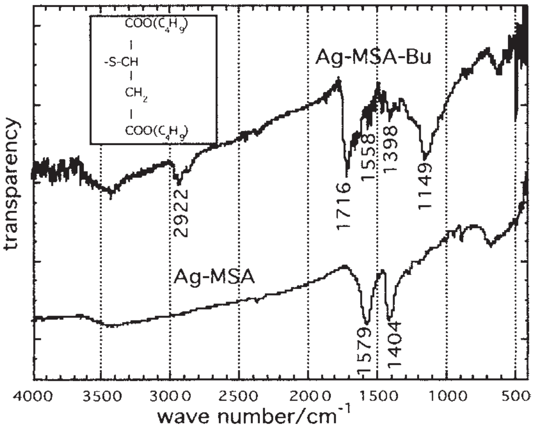

Figure 4. FT-IR spectra of Ag-MSA and Ag-MSA-Bu samples.

In order to examine the content of unmodified carboxylate groups on the surface, we have conducted the energy dispersive X-ray analysis (EDX). The result of area analysis ($100 \times 100\,\mu\mathrm{m}^2$) is listed in Table 1. Since the surface carboxylate group is either $-\mathrm{COONa}$ or $-\mathrm{COO(C_4H_9)}$, the most important elements to be analyzed are C and Na. The initial atomic ratio of C and Na, 4 : 2, changes to 12 : 0 if complete esterification takes place. Hence C : Na $= 12 - 4x : x$, in which x is Na atomic content. We have found that the conversion rate of esterification was 98%. That is to say, almost of all surface carboxylate were converted to ester. To show directly this estimate, we have suspended two samples, Ag-MSA powders and Ag-MSA-Bu powders, into water/n-butanol mixed solution. The photograph is shown in Figure 5. It goes without saying that the surface character of Ag particles was quantitatively modified through esterification.

Table 1. Energy dispersive X-ray analysis of Ag-MSA-Bu powders. Units in atom%

C	O	Na	S	Sum
56.14	20.05	0.87	9.63	86.69

The Sum is less than 100 because of subtraction of background signals from substrate.

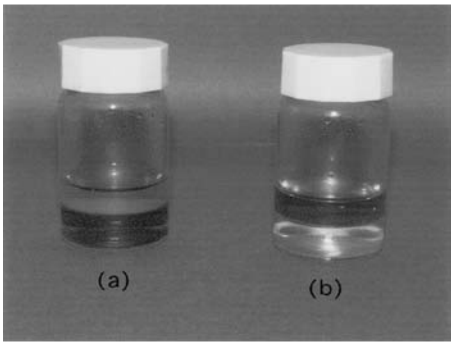

Figure 5. Photo of the dispersions; a) before and b) after esterification. Note that the upper layer is n-butanol and the lower is water for both bottles.

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