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Preparation of Electrically Conductive Film from Silver Nanocolloid Synthesized by Reduction of Silver–Thiolate

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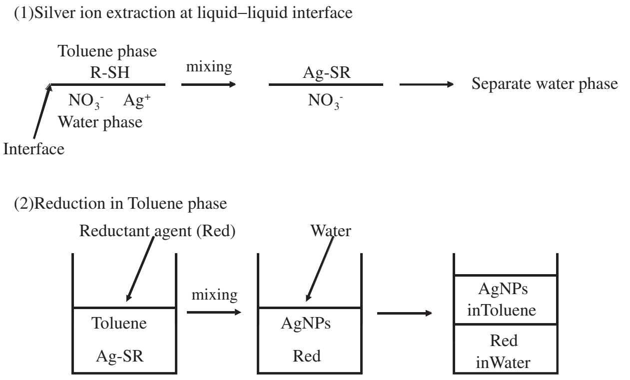
We have developed a simple scheme for preparation of silver nanoparticle film. This scheme includes the reaction between octanethiol in the toluene and silver ion in water at toluene–water interface. The electric conductive films would be produced by sintering the coated films of the prepared silver nanoparticles below 200 °C.

Silver nanoparticle films have been extensively studied in many fields including microelectronics,[1,2] optics,[3,4] catalysis,[5,6] and sensing.[7,8] Numerous procedures for the synthesis of Ag nanoparticles have consequently been developed.[9–14] Chemical reduction[12–14] is one of the most widely studied procedures. In this procedure, extraneous materials such as excess reductants and counter ions need to be removed from the reaction system to purify the obtained suspension after the synthesis of Ag nanoparticle film. However, it is extremely difficult to remove these extraneous materials from the suspension due to the difficulty of solid–liquid separation. Although conventional solid–liquid separation techniques such as centrifugation and membrane separation can be efficiently applied to suspensions of submicron- or micron-sized materials, they are not yet considered to be efficient for the separation of nanoscale materials due to high cost and/or low speed. One of the more promising approaches for the development of a new scheme for nanocolloid preparation with low cost and low energy consumption is a two-phase liquid–liquid method. The most widely known case of successful preparation of nanoparticles using this method was reported[15] for the preparation of fine gold nanoparticles (AuNPs). In this method, nanoparticle preparation is carried out in a toluene/water system. First, $AuCl_4^-$ is extracted from the water phase to the toluene phase by complexation with a phase-transfer agent (tetraoctylammonium bromide: TOAB). The extracted Au ions are protected with alkanethiol as a capping agent. Thiol-protected AuNPs are then formed by the reduction of Au ions with $NaBH_4$, in which TOAB also acts as a phase-transfer agent to extract the reductant ions. As a result, AuNPs are formed in the toluene phase, and the extraneous materials remain in the water phase. In other words, this is a one-step preparation method incorporating both the synthesis and purification processes. Attempts have been made to extend this procedure to the synthesis of Ag nanoparticles.[16,17] However, TOAB is a cationic surfactant, so that it hardly transfers Ag^+ ions into an organic solvent. If extraction of the metal ions can be performed with a capping agent, a simple preparation procedure using minimal agents (metal ion, capping agent, and reductant) could be developed. In this paper, we report on the preparation of Ag nanoparticle film by reduction of silver thiolate[18,19] prepared by Ag ion extraction with a capping agent.



Scheme 1. Strategy of silver nanoparticle film preparation.

The strategy is illustrated in Scheme 1. This method is based on the two-phase liquid–liquid reaction using toluene and water. First, Ag ions are extracted from the water phase to the toluene phase by complexation with alkanethiol as a capping agent. Thiol-protected Ag nanoparticle film is then formed in the toluene phase through reduction of the silver complex with hydrophilic reductant. Excess reductant is easily removed by water extraction. Details of the procedure used in the present study are described below. Octanethiol (63.5 µL) and toluene (5 g) were mixed with a magnetic stirrer. An aqueous solution of silver nitrate (0.25 M, 1.48 mL) was added to the thiol–toluene solution, and the two-phase liquid–liquid mixture was stirred for 5 min. During stirring, the color of the toluene phase changed to pale yellow, indicating silver–alkanethiol complex formation. After stirring, the water phase was removed from the two-phase mixture. A methanol solution of sodium borohydride (0.44 M, 1 mL) was mixed with the pale-yellow toluene separated from the two-phase mixture. During stirring, the color of the mixture changed to brown. After stirring, the brown solution was shaken with ion-exchanged water (5 mL) to remove unreacted reductant. After about 1 min of shaking, the solution spontaneously separated into the water and toluene phases and then the water phase was removed. The residual reductant removal procedure was repeated three times. The prepared Ag nanoparticle films were characterized using transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetry–mass spectrometry (TG-MS), energy-dispersive X-ray spectrometry (EDS), and X-ray diffraction (XRD).

TEM observation of the prepared nanoparticles (Figure 1) showed a mean diameter of approximately 5.5 nm and a coefficient of variation (CV) of 27%. In the IR spectrum of the prepared nanoparticles (Supporting Information; SI, Figure S1[20]), the peak of the thiol group was found around 2900 cm^{-1}, indicating that the surfaces of the prepared Ag nanoparticle film were capped with octanethiol. In the XRD pattern (Figure S2[20]), no peaks of bulk silver were observed. Thus, the formed Ag nanoparticles are considered to be

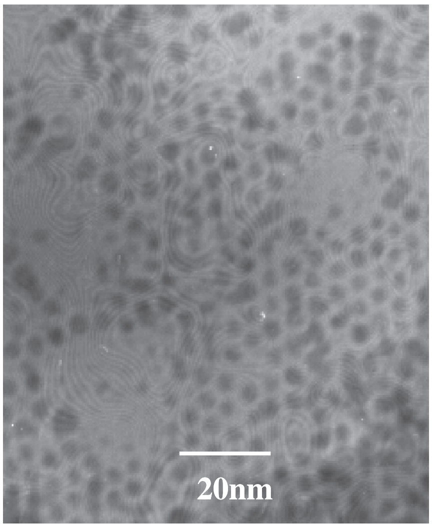


Figure 1. TEM micrograph of prepared silver nanoparticle film.

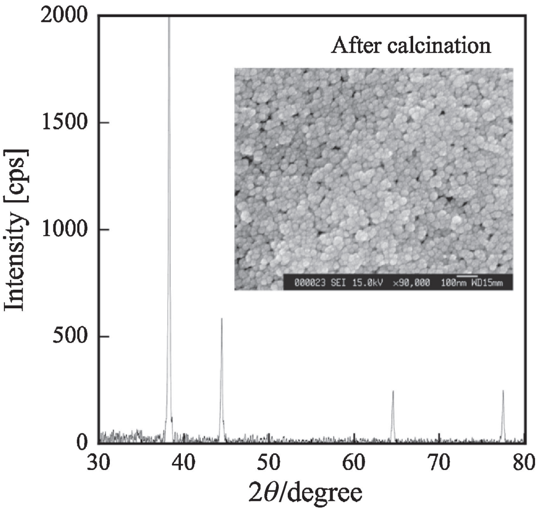


Figure 2. XRD pattern of sintered nanoparticle film at 200 °C (inset in SEM image).

amorphous. In the TG curve of the prepared nanoparticles (Figure S3[20]), a drastic decrease in weight was observed at around 200 °C, which corresponds to the boiling point of dodecanethiol. This indicates that octanethiol molecules adsorbed on the surfaces of the Ag nanoparticles became detached from the Ag nanoparticle surfaces. A mirror-like silver metal film was formed by sintering Ag nanoparticle film at 200 °C in air. The silver mirror is electrically conductive and its XRD pattern has an fcc lattice structure (Figure 2). In mass spectrum measurement, m/z peaks of 145 and 290 (corresponding to $C_8H_{17}S$ and $(C_8H_{17}S)_2$, respectively) appeared (Figure S4[20]). The existence of Ag ions in the water phase separated as shown in Scheme 1(1) was qualitatively examined by adding aqueous HCl solution. No precipitate was formed in the water phase. This simple result implies that Ag ions in the water were completely extracted by alkanethiol. Furthermore, the extraction with thiol was very rapidly accomplished, within 5 min. To check the content of residual materials in the prepared suspension of Ag nanoparticles, Ag nanoparticle powder film obtained from the suspension by evaporating toluene was analyzed by EDS. As shown in Table S1,[20] only trace amounts of extraneous (residual) materials were found to exist in the Ag nanoparticle film. This result indicates that extraneous materials were easily removed simply by mixing with water in the procedure.

In summary, the preparation of Ag nanoparticle film by phase transfer through a liquid–liquid interface with a capping agent has, therefore, been demonstrated to be feasible. The preparation technique described here has two advantages. First, Ag nanoparticles can be prepared using only minimum reagent in the chemical reduction method, a silver ion source, a particle stabilizer, and a reductant. Second, no equipment for particle separation is necessary, because the extraneous materials can be easily removed by water extraction. This procedure requires only mixing equipment. These two advantages may facilitate the mass production of Ag nanoparticle film. The Ag nanoparticle film prepared using this procedure become metallized at 200 °C.

The metallized particles have an fcc structure and electrical conductivity. Therefore, the prepared Ag nanoparticle film was suitable for use as electrodes in applications such as printed circuit boards.

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20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.