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Direct Transformation into Silver Nanoparticles via Thermal Decomposition of Oxalate-Bridging Silver Oleylamine Complexes

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Silver(I) oxalate, $Ag_2(C_2O_4)$, reacts with two equivalents of oleylamine (Ag:oleylamine = 1:1 mole/mole) to form an oxalate-bridged silver-oleylamine complex, [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)]. The precursor complex is thermally decomposed at ~150 °C with CO_2 evolution to produce Ag nanoparticles with ~11 nm dimension. The Ag nanoparticles contain ~12 wt% of oleylamines as the surface stabilizer. In the synthetic mechanism, the oxalate ligand acts as a two-electron reducing agent. The precursor complex is directly transformed into oleylamine-stabilized Ag nanoparticles in high yields of more than 80% without any additional synthetic organic solvents and reducing agents.

Keywords: Silver Nanoparticle, Oleylamine, Oxalate Complex, Thermal Decomposition, Auto Redox Reaction.

1. INTRODUCTION

The exhaustion of rare metals and mineral oils is an increasingly serious global problem. In spite of technological advances, a large amount of the metal resources has been discarded in metallic fine-patterning processes such as photolithography for electronic devices. The rapid progress of ink-jet printing techniques will revolutionize the process of manufacturing electronic devices.[1–3] Ink-jet printing greatly contributes to saving materials, because the amount of ink needed can be applied on designed and limited areas on various substrates. The advent of such printed electronics has prompted to synthesize stably dispersed metallonanoparticles in various solvents as "metallonanoparticle inks." Industrial applications of the metallonanoparticle inks necessitate the development of their simple, low-cost, large-scale, and green syntheses, which will achieve high yields based on the metal precursors, drastically reduce synthetic organic solvents and surfactants, and remove harmful chemicals.[4,5]

Metallonanoparticles have fascinating natures related to their size-dependent electronic structures and extremely large surfaces. In particular, there has been growing interest in Ag nanoparticle inks as a printable material. The easy rearrangement of the surface Ag(0) atoms of nanoparticles initiates low-temperature sintering among them, leading to high electrical conductivity. In alkylamine-stabilized Ag nanoparticles, the neutral alkylamines are weakly bound to the Ag(0) surface. Therefore, the alkylamines can be readily removed from the surface by exposure to methanol,[6] and displaced with the other surfactants.[7] The Ag nanoparticles lose their surface alkylamines and can be densely sintered on substrates at low temperatures, showing excellent low resistivities.[6,8] Because of such facile elimination and displacement of the weakly bound alkylamines, the alkylamine-stabilized Ag nanoparticles are among the most useful candidates for low-temperature sintering materials, realizing fine printed circuits on organic polymer substrates that are unstable at temperatures above 150 °C. There has been also increasing importance of alkylamine-stabilized Au, Pt, Pd, and Cu nanoparticles,[9–13] which will show higher catalytic performance of their zero-valent surfaces bearing the neutral surfactants.

The thermal reactions between alkylamine and Ag^+ have provided alkylamine-stabilized Ag nanoparticles.[6,7,14] The simple synthesis of oleylamine-stabilized Ag nanoparticles was reported by Hiramatsu and Osterloh.[7] In refluxing a large amount of hexane, toluene, and 1,2-dichlorobenzene containing silver acetate

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and excess oleylamines, oleylamine-stabilized Ag nanoparticles were produced in yields of 11.3, 10.9, and 14.3%, respectively. The microreactor synthesis of oleylamine-stabilized Ag nanoparticles was performed using silver acetate:oleylamine = 1:25 mole/mole dissolved in 1,2-dichlorobenzene according to Hiramatsu and Osterloh's procedures.[14] Dodecylamine-stabilized Ag nanoparticles were also prepared by heating a mixture of $[Ag^I(dodecylamine)_2]NO_3$:dodecylamine = 1:4 mole/mole at ~200 °C.[6] The thermal syntheses of the alkylamine-stabilized Ag nanoparticles have resulted in lower yields. Silver acetate was reduced using phenylhydrazine in a toluene solution of alkylamines to quantitatively yield alkylamine-stabilized Ag nanoparticles. However, phenylhydrazine is one of harmful chemicals which changes into benzene after the reaction.[8] In these limited syntheses of the alkylamine-stabilized Ag nanoparticles, excess amounts of organic solvents and surfactants, along with additional harmful reducing agents, have been required.

The other surfactant-stabilized Ag nanoparticles have been prepared in combinations of silver salts and reducing agents, e.g., combinations of silver nitrate or silver carboxylates and ascorbic acid,[15] borohydrides,[16] polyols,[17] aldehydes,[18] or hydrazines.[19] Through the thermal reaction between silver alkylcarboxylates and an equimolar amount of alkylamines, Ag nanoparticles stabilized by mixed surfactants of alkylcarboxylate and alkylamine have been prepared in high yields (67–90%).[20] This pioneering synthesis requires essentially no synthetic organic solvents. Thermal syntheses of alkylcarboxylate-based Ag nanoparticles have resulted in much higher yields[5, 20–22] than those of alkylamine-based Ag nanoparticles.[6, 7, 14]

In this study, we adopt an oxalate ion, $C_2O_4^{2-}$ as an inexpensive reducing agent. We report the simple, low-cost, large-scale, and high-yield synthesis of oleylamine-stabilized Ag nanoparticles. Silver(I) oxalate, $Ag_2(C_2O_4)$, reacts with two equivalents of oleylamine (Ag: oleylamine = 1:1 mole/mole) to form an oxalate-bridged silver-oleylamine complex, $[(oleylamine)Ag(\mu\text{-}C_2O_4)Ag(oleylamine)]$. The precursor complex is thermally decomposed at ~150 °C with CO_2 evolution to produce oleylamine-stabilized Ag nanoparticles of ~11 nm dimension. In the synthetic mechanism, the oxalate ligand acts as a two-electron reducing agent. The solid precursor complex is directly transformed into oleylamine-stabilized Ag nanoparticles in high yields of more than 80% without any additional organic solvents and reducing agents.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Silver(I) Oxalate, $Ag_2(C_2O_4)$

From an aqueous mixture of stoichiometric Ag^+ and $C_2O_4^{2-}$, $Ag_2(C_2O_4)$ was precipitated quantitatively. The powder X-ray diffraction (XRD) pattern was consistent with those of JCPDS file (No. 22-1335) and previous reports (Fig. 1(A)).[23] The results of thermogravimetric/differential thermal analysis (TG/DTA) of $Ag_2(C_2O_4)$ under air showed that an exothermic reaction occurred at 199 °C, accompanied by a sharp weight drop around 71%. The weight loss corresponded to the thermal auto-redox reaction of $Ag_2(C_2O_4)$, as shown in Eq. (1).

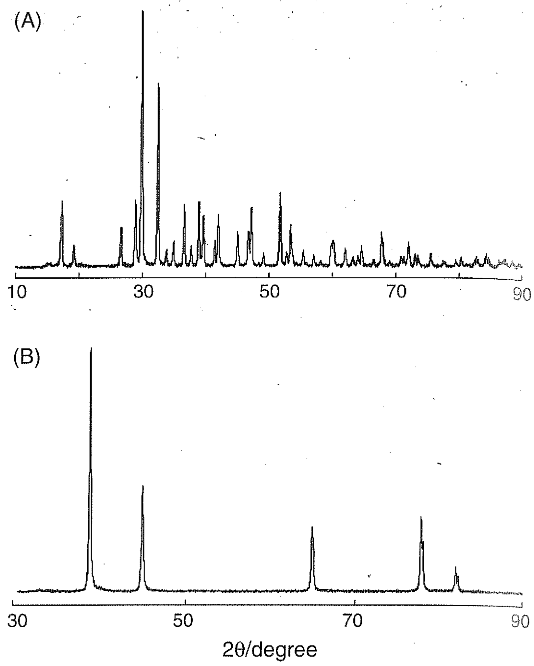

Fig. 1. XRD patterns of (A) $Ag_2(C_2O_4)$ and (B) the thermally decomposed product of $Ag_2(C_2O_4)$ at 250 °C for 30 min under air.

$$Ag_2^I(C_2O_4) \rightarrow 2Ag^0_{(s)} + 2CO_{2(g)} \uparrow \qquad (1)$$

Metallic silver was readily produced through the thermal decomposition of $Ag_2(C_2O_4)$ at 250 °C in an electric furnace under air, based on the XRD pattern (Fig. 1(B)). Aggregated Ag nanoparticles of various sizes (10–200 nm) have been formed by the explosion-like decomposition of $Ag_2(C_2O_4)$ with the evolution of CO_2 gas.[24] The classic metal oxalates and related complexes make up a new and useful precursor family for fabricating metal and metal oxide nanomaterials. The main advantages of $Ag_2(C_2O_4)$ as a useful precursor of Ag nanomaterials are that

(i) $Ag_2(C_2O_4)$ is quantitatively obtained from an aqueous mixture of $AgNO_3$ and $(NH_4)_2C_2O_4$ or $H_2C_2O_4$, which is inexpensive and a component of nature;
(ii) the auto-redox reaction (Eq. (1)) proceeds at a temperature under 200 °C;
(iii) silver metals are obtained via the solid-state reaction of $Ag_2(C_2O_4)$ under air without any synthetic solvents;
(iv) a by-product, CO_2, derived from the self-reducing agent, $C_2O_4^{2-}$, is released from the product;
(v) the coordination polymer crystal, $Ag_2(C_2O_4)$, with infinite oxalate-bridging structures[25, 26] of Ag^+ can be transformed into an oxalate-bridged discrete complex,

$[(X)_m Ag(\mu\text{-}C_2O_4)Ag(X)_m]$ by the addition of a neutral ligand, X.[27]

2.2. Isolation of an Oxalate-Bridged Silver-Oleylamine Complex

In our attempt to realize the simple, low-cost, large-scale, and high-yield synthesis of oleylamine-stabilized Ag nanoparticles, a discrete complex, $[(\text{oleylamine})Ag(\mu\text{-}C_2O_4)Ag(\text{oleylamine})]$, was adopted as a precursor instead of the coordination polymer, $Ag_2(C_2O_4)$. To isolate the precursor complex, an excess of oleylamine (Ag:oleylamine = 1:2 mole/mole) was employed. To accelerate the coordination reaction between oleylamines and $Ag_2(C_2O_4)$, a mixture of water and methanol was used for the synthetic solvent of the precursor complex, probably mediating the hydrophobic nature of the hydrocarbon chains of the oleylamines and the hydrophilic nature of $Ag_2(C_2O_4)$. There are two types of the coordination reactions between $Ag_2(C_2O_4)$ and alkylamines. In Ag:alkylamine = 1:1 and 1:2 (mole/mole) reaction conditions, $[(\text{alkylamine})Ag(\mu\text{-}C_2O_4)Ag(\text{alkylamine})]$ and $[Ag(\text{alkylamine})_2]_2(C_2O_4)$ may be formed, respectively. Even in the Ag:oleylamine = 1:2 reaction condition, the isolated white solid contained one equivalent of oleylamine, the composition of which was consistent with that of $[(\text{oleylamine})Ag(\mu\text{-}C_2O_4)Ag(\text{oleylamine})]$, based on the TG/DTA weight loss. From the ESI-mass spectrum, the complex moiety of $[Ag(\text{oleylamine})]^+$ of $[(\text{oleylamine})Ag(\mu\text{-}C_2O_4)Ag(\text{oleylamine})]$ was detected at 374 m/z without $[Ag(\text{alkylamine})_2]^+$. Similar oxalate-bridged Ag dinuclear complexes such as $[((n\text{-Bu})_3P)_m Ag(\mu\text{-}C_2O_4)Ag((n\text{-Bu})_3P)_m]$ ($m = 1, 2, 3$) were reported. They were formed from the reaction of $Ag_2(C_2O_4)$ and two to six equivalents of $(n\text{-Bu})_3P$.[27]

2.3. Synthesis of Oleylamine-Stabilized Silver Nanoparticles

To simplify the synthetic procedures of the oleylamine-stabilized Ag nanoparticles, the as-formed precursor complex, $[(\text{oleylamine})Ag(\mu\text{-}C_2O_4)Ag(\text{oleylamine})]$, was heated without isolation from the reaction solvent, and vigorous gas evolution occurred up to 150 °C. The gas was recognized as CO_2 based on the observation of the white precipitation of $CaCO_3$ when the gas was passed through the limewater. In the reaction period of the CO_2 evolution for ten or several tens of minutes, the precursor complex was drastically changed into a blue luster solution. Blue luster solids were isolated from the reaction solution. The XRD pattern of the blue luster solids exhibited a face-centred cubic structure of silver crystals (Fig. 2). The Ag particle dimension was estimated as 4.3 nm from the XRD half-widths based on the Scherrer's equation. Two-dimensional superlattice domains of the Ag nanospheres were observed on transmission electron microscopy (TEM) images (Fig. 3(A)). Based on the TEM image, the estimated number-averaged particle size was 11.3 ± 1.1 nm (Fig. 3(B)). As estimated from the XRD line broadening, the apparent TEM particle size was much

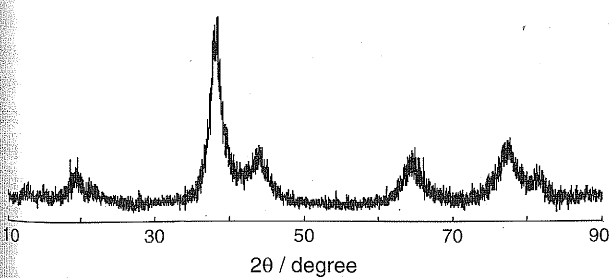

Fig. 2. XRD pattern of the blue luster solids of the oleylamine-stabilized Ag nanoparticles.

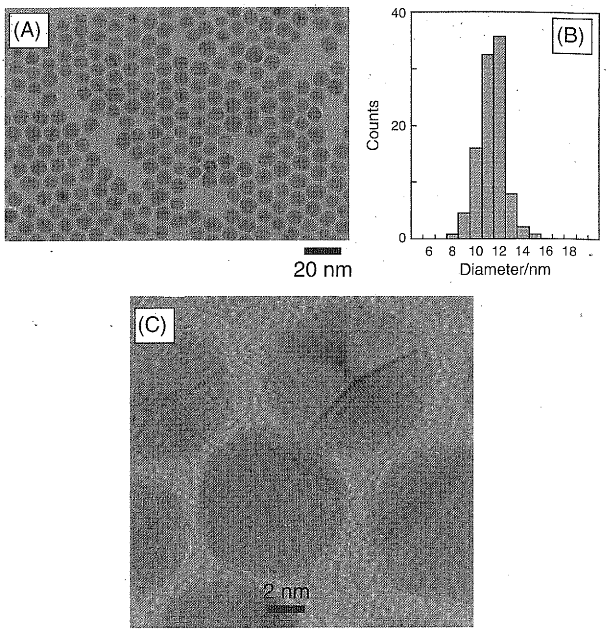

Fig. 3. (A) TEM image, (B) size distribution, and (C) HRTEM image of the oleylamine-stabilized Ag nanoparticles.

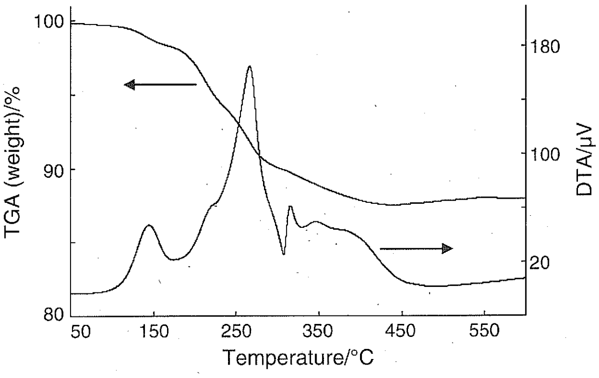

Fig. 4. TG/DTA profile of the blue luster solids of the oleylamine-stabilized Ag nanoparticles under air.

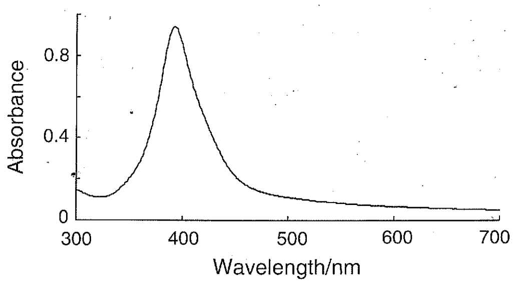

Fig. 5. UV-vis absorption spectrum of the hexane dispersion solution of the oleylamine-stabilized Ag nanoparticles (8.0 μg/mL).

larger than 4.3 nm. The XRD line broadening generally reflects the single crystalline particulate size. Therefore, the inconsistency between the XRD and TEM particle sizes is relevant in the case of polycrystalline particles containing lattice defects.[22] In fact, such lattice defects have been observed as discontinuous lattice images of some Ag nanoparticles in high-resolution TEM (HRTEM) measurements (Fig. 3(C)).[6,28] The lattice spacing is ~0.24 nm, which is consistent with that of the (111) plane of the silver crystal. In the two-dimensional superlattice structure on the TEM image (Fig. 3(A)), the interparticle spaces are partially filled with oleylamines as a surface stabilizer of each Ag nanosphere.[29] In the TG/DTA profile of the blue luster solids, the maximal weight loss was ~12 wt% over 400 °C under air (Fig. 4). Based on the XRD pattern, the blue luster solids were thermally changed into white luster solids of metallic silver at 400 °C under air. Therefore, the thermal elimination of oleylamines chemisorbed on the Ag nanoparticles was responsible for the TG/DTA weight loss of ~12 wt%. Oleylamine-stabilized Ag nanoparticles can be synthesized in high yields of more than 80% based on the silver contents (~88 wt%) calculated from the weight loss. The oleylamine-stabilized Ag nanoparticles of the blue luster solids were redispersed in hexane, and ultraviolet-visible (UV-vis) absorption spectra of the dispersion solution showed an intense absorption band in a narrower range between 350 and 450 nm due to the specific surface plasmon band of the Ag nanospheres (Fig. 5).[7] In dynamic light-scattering (DLS) measurements of the dispersion solution (0.50 mg (oleylamine-stabilized Ag nanoparticle)/mL (hexane)), the number-averaged particle size was 14 ± 2 nm at 20 °C, near that of the TEM image.

In a possible formation mechanism of the oleylamine-stabilized Ag nanoparticles, the thermal decomposition of [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)] leads to an intermediate of an oleylamine-coordinated dinuclear Ag(0) cluster through the elimination of the bridging oxalate ligand as CO_2 gases (Eq. (2)).

$$[(\text{oleylamine})\text{Ag}^{\text{I}}(\mu\text{-C}_2\text{O}_4)\text{Ag}^{\text{I}}(\text{oleylamine})] \rightarrow [(\text{oleylamine})\text{Ag}_2^0(\text{oleylamine})] + 2\text{CO}_{2(g)}\uparrow \quad (2)$$

The oleylamine ligands could not fully stabilize such small Ag(0) clusters. The Ag(0) cluster intermediates grew into ploycrystalline nanoparticles of ~10 nm dimension via the successive combination of the intermediates. The addition of excess oleylamines between four and eight equivalents did not contribute to notable increases in the Ag nanoparticles in the yield. The chemisorbed oleylamine molecules were 5.5 mole% of Ag in the Ag nanoparticle, as estimated from the TG-DTA weight loss of 12%. This fact indicates that 94.5 mole% of the oleylamine ligands of [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)] became free from Ag after the complete transformation into Ag nanoparticles. Therefore, the Ag nanoparticles could be prepared with excess oleylamines even in the decomposition of [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)]. The Ag(μ-C_2O_4)Ag moieties of the precursor complexes are discrete from each other by the termination of two oleylamines, unlike the coordination polymer structure of $Ag_2(C_2O_4)$. It is thought that the binuclear Ag(0) clusters can be protected by vicinal oleylamines simultaneously after the thermal decomposition of the Ag(μ-C_2O_4)Ag moiety, as shown in Eq. (2). Such oleylamines densely surrounding the Ag(0) cluster intermediates successfully inhibit excessive crystal growth to larger insoluble Ag particles, leading to more than 80% yields of oleylamine-stabilized Ag nanoparticles.

Very recently, by Viswanath et al., polyvinyl alcohol (PVA)-protecting Ag nanoparticles have been prepared via the thermal decomposition of $Ag_2(C_2O_4)$ in PVA;[30] however, an oxygen-free atmosphere was necessary for the initial chemical reduction with PVA and the subsequent auto-redox reaction of the coordination polymer solids, $Ag_2(C_2O_4)$.[30,31] Due to the difference of the capping agent, the advantages of this work against the Viswanath's one may be in the easy fabrication of the conductive silver film from the obtained nanoparticles by heating only at rather low temperatures.

3. CONCLUSION

We succeeded in the simple, low-cost, large-scale, and high-yield synthesis of oleylamine-stabilized Ag nanoparticles by the thermal decomposition of a solid precursor complex, [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)], without any additional reducing agents at a moderate temperature around 150 °C. In the syntheses, we achieved no inert gas atmospheres, essentially no synthetic organic solvents, and minimum consumption of the surfactants, oleylamine, but we used a small volume of methanol in preparing the precursor complex. After the thermal decomposition of the precursor complex, the oleylamine-stabilized Ag nanoparticles were dispersed in liquid oleylamines released from the precursor complexes without contamination of by-products derived from the reducing agent of $C_2O_4^{2-}$. Isolation and purification of the oleylamine-stabilized Ag nanoparticles from the liquid oleylamines were carried out by simple filtration and precipitation upon the addition of small volumes of hexane and methanol, respectively. The organic waste containing oleylamines could be recycled to re-synthesize the oleylamine-stabilized Ag nanoparticles.

High-yield syntheses of other alkylamine-based Ag nanoparticles and the development of low-temperature sintering nanomaterials using lower-boiling-point alkylamines, such as octylamine, are in progress. In our preliminary results, spin-coated films of the Ag nanoparticles stabilized by lower-boiling-point alkylamines were transformed into a silver mirror through low-temperature sintering among the nanoparticles at less than 150 °C. High electric conductivity on organic polymer substrates was achieved. A detailed report will appear in the next article.

4. EXPERIMENTAL DETAILS

4.1. Materials

Silver(I) nitrate and ammonium oxalate monohydrate were purchased as extra pure grades from Kanto Chemicals. Oleylamine was supplied from Acros Organics (80–90% purity) and Kao Chemicals (72% purity). All reagents were used without further purification.

4.2. Synthesis

4.2.1. Synthesis of Silver(I) Oxalate, $Ag_2(C_2O_4)$

Silver oxalate was prepared according to the literature.[25] An aqueous solution (50 mL) of $AgNO_3$ (34.0 g, 0.200 mol) was added to an aqueous solution (150 mL) of $(NH_4)_2(C_2O_4) \cdot H_2O$ (17.1 g, 0.120 mol) with stirring for 1 hr. The reaction mixture stood for 1 day. The resulting white precipitate was filtered with suction, washed with water three times, and then dried under reduced pressure to yield $Ag_2(C_2O_4)$ (30.3 g, 99.7%). All procedures were carried out in the dark to avoid the photolysis of $Ag_2(C_2O_4)$.

4.2.2. Isolation of an Oxalate-Bridged Silver-Oleylamine Complex

$Ag_2(C_2O_4)$ (6.08 g, 20.0 mmol) was added to a mixture of oleylamine (21.4 g, 80.0 mmol), methanol (20 mL), and water (8 mL) and then stirred for 1 day in the dark. The as-formed white product was centrifuged and washed with diethyl ether twice in order to remove excess oleylamines and then was dried under air in the dark. The isolated product was unstable and gradually decomposed into a brown viscous solid. The silver content of the isolated product was 24.9 wt% based on a TG/DTA profile near that (25.7 wt%) of [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)]. The following spectra were observed: ESI-mass spectrum (JEOL JSM-700): 374 m/z as $[Ag(oleylamine)]^+$; FT-IR spectrum (Jasco FT/IR-4100): ν_{NH} (oleylamine) 3424, ν_{CH} (oleylamine) 2917 and 2848, and δ_{NH} (oleylamine) 1597 cm^{-1} superposed on ν_{CO} (oxalate ion).

4.2.3. Synthesis of Oleylamine-Stabilized Silver Nanoparticles

$Ag_2(C_2O_4)$ (6.08 g, 20.0 mmol) was added to a mixture of oleylamine (10.7 g, 40.0 mmol), methanol (20 mL), and water (8 mL) and then stirred for 1 day in the dark. During the reaction period, the white solids of $Ag_2(C_2O_4)$ disappeared, and the reaction mixture was changed into a white emulsion. After the evaporation of methanol and water at 40 °C under reduced pressure, a white residue of an oxalate-bridged silver-oleylamine complex, [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)], was obtained. In order to initiate the thermolysis of [(oleylamine)Ag(μ-C_2O_4)Ag(oleylamine)] with the vigorous evolution of CO_2 gas, the white residue was gradually heated up to 150 °C, and the thermolysis of the precursor complexes was terminated within several tens of minute. The reaction temperature was further maintained for 10 min after completion of the CO_2 evolution. The resulting blue luster solution was allowed to cool to room temperature. Upon the addition of methanol (20 mL) to the solution, Ag nanoparticles were immediately precipitated and centrifuged. The sediment was re-dispersed in a minimum volume of hexane ($\leq$40 mL) to afford a deep reddish-yellow dispersion. After centrifugation, the supernatant was filtered through a 0.50 μm-pore membrane. After the addition of methanol ($\leq$20 mL) to the filtrate, the precipitated blue luster solids of the oleylamine-stabilized Ag nanoparticles were centrifuged and dried under reduced pressure in a yield of 3.99 g (82.1% based on the silver content). The silver content of the oleylamine-stabilized Ag nanoparticles was estimated as 88.1 wt% by thermogravimetric/differential thermal analysis (TG/DTA).

4.3. Measurements

Powder X-ray diffraction (XRD) analyses were performed using a Rigaku MiniFlex II desktop X-ray diffractometer (Cu Kα_1 radiation). Transmission electron microscopy (TEM) images of the Ag nanoparticles were observed using a Hitachi High-Tech H-9500 (300 keV). For the TEM samples, a hexane dispersion solution of the Ag nanoparticles was dropped on ultrathin amorphous carbon films supported by Cu grids and dried under air. Ultraviolet-visible (UV-vis) absorption spectra of dispersion solutions of the Ag nanoparticles were recorded on a Shimadzu UV-3150 UV/VIS-NIR spectrophotometer. The dynamic light-scattering (DLS) particle sizes of the Ag nanoparticles were measured on an

Otsuka ELS-Z2M particle size and zeta-potential analyzer. Thermogravimetric/differential thermal analyses (TG/DTA) were performed using a Shimadzu DTG-60.

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