

Roles of Chloride Anions in the Shape Evolution of Anisotropic Silver Nanostructures in Poly(vinylpyrrolidone) (PVP)-Assisted Polyol Process

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The roles of Cl^- ions on the shape evolution of various silver (Ag) nanostructures including cubes, triangular bipyramids, and rods/wires in AgNO_3 /poly(vinylpyrrolidone) (PVP)/ethylene glycol (EG) solution have been investigated by changing the concentration of added NaCl, the reaction solution temperature, and the temperature of injection of NaCl to the original AgNO_3 /PVP/EG solution under oil-bath heating. The addition of different amounts of NaCl could tune morphologies and sizes of the final products from spheres via cubes to rods/wires. Reaction temperature decided the reduction power and the yield of bipyramids increased with decreasing the reaction temperature from 198 to 120 °C. Changing the solution temperature at which NaCl was introduced into the solution could effectively influence the yields of different Ag structures by adjusting the ratios of Ag and AgCl seeds formed in the solution. We found that AgCl could be an important precursor for the formation of the Ag cubes and bipyramids. The roles of Cl^- anions for the evolution of various Ag nanostructures have been discussed by taking account of the formation of AgCl as seeds, selective adsorption of Cl^- on {100} facets of Ag nanoparticles, and oxidative etching of the Ag particles by Cl^-/O_2 .

Recently, Ag nanostructures have attracted considerable attention mainly due to their remarkable optical properties and numerous applications in fields such as catalysis, surface plasmonics, surface-enhanced Raman scattering, and chemical or biological sensing.^{1–3} Since chemical and physical properties of the Ag nanocrystals are highly related to orientations of various crystalline surfaces, the controllable preparation of Ag nanocrystals with different shapes and exposed surfaces is very important and challengeable.

Polyol reduction is a typical technique for the preparation of Ag nanocrystals by reducing Ag^+ ions in the presence of a polymer surfactant such as poly(vinylpyrrolidone) (PVP) in ethylene glycol (EG).⁴ We have carried out a systematic study of the synthesis of Ag nanostructures by the polyol method under microwave (MW) and oil-bath heating.⁵ There are two purposes in our studies. One is to develop a rapid shape and size control synthesis method for Ag nanostructures. The other is to understand the mechanism of the formation of various Ag nanostructures in the polyol reduction. In a previous paper, we examined the effects of bubbling gas and found that bubbling O_2 gas into the reacting solution facilitated the formation of monodispersed Ag nanowires with a high yield (>90% without isolation).^{5f}

Wiley et al.⁶ prepared single-crystal cubes and tetrahedrons of silver with truncated corners/edges in high yields by reducing AgNO_3 with EG heated to 148 °C in the presence of PVP and a trace amount of NaCl. It took more than 45 h to prepare

these truncated Ag nanocrystals. We have also found that the presence of Cl^- anions is necessary for the preparation of such anisotropic Ag nanostructures as cubes, bipyramids, and nanowires with sharp corners/edges in the polyol process.⁵ However, optimum conditions for preparing each kind of different anisotropic Ag nanostructure have not been obtained under oil-bath heating. In this work, to determine the optimum conditions for the preparation of each anisotropic Ag nanostructure under oil-bath heating and to clarify roles of Cl^- such as the formation of AgCl seeds, adsorption of Cl^- to specific facets of Ag nanoparticles, and shape-selective etching of Ag nanoparticles by Cl^-/O_2 , we examined the dependence of shapes and sizes of the anisotropic Ag nanostructures on the concentration of added NaCl, the solution temperature, and the injection temperature of NaCl to the original AgNO_3 /PVP/EG solution. We discuss the roles of Cl^- anions for the preparation of these anisotropic Ag nanostructures in the polyol experiments.

In general, Ag nanostructures can be prepared under both oil-bath and rapid MW heating. An advantage of the oil-bath heating is that the temperature of reaction solution increases more slowly than that under MW heating. Furthermore, the reaction flask is open to outside. Therefore, taking the reacting solution sample in each reaction stage, that is necessary for evaluating the growth mechanism of the Ag nanostructures, is easy. This is a major reason why the oil-bath heating method has been used to preparing the Ag nanostructures in the present study.

Experimental

Materials. AgNO_3 (99.8%), NaCl (99.5%), and EG (99.5%) used for this study were purchased from Kishida Chemical Industries Ltd. The PVP powder (average molecular weight in monomer units, MW: 40000) was purchased from Wako Pure Chemical Industries Ltd. All these reagents were used without further purification.

Effect of Concentration of NaCl. First, 17.4 mL EG solution containing 0.585 g PVP (MW: 40000) and 0.6 mL NaCl solution (0–15 mM in EG) were placed in a 100 mL three-necked flask to form a homogeneous solution. Then, 2 mL AgNO_3 solution (0.465 M in EG) was added to the above solution. The concentrations of AgNO_3 , NaCl , and PVP in EG were 46.5, 0–0.45, and 264 mM, respectively. The mixture was heated from room temperature (20 °C) to the boiling point of EG (198 °C) in an oil bath. Magnetic stirring was applied throughout the entire synthesis in this work. After the reaction finished, the system was naturally cooled to room temperature.

Effect of AgCl. First, 19.1 mL EG solution containing 0.585 g PVP (MW: 40000) and 0.6 mL NaCl (0.01 M in EG) was placed in a 100 mL three-necked flask. Then, 0.3 mL AgNO_3 solution (0.02 M in EG) was added to the resulting solution. Finally, the mixture including equal molar NaCl (0.3 mM) and AgNO_3 (0.3 mM) was heated from room temperature to 198 °C in an oil bath and kept it at 198 °C for 10 min.

Effect of Temperature at a Constant NaCl Concentration. The experimental procedure used for studying the effect of temperature at a constant NaCl concentration was similar to that described in “Effect of concentration of NaCl ” except for the final temperature. After reaction solutions were heated to 120 and 148 °C, solutions were kept at the same temperatures for 1–2.5 h.

Effect of Addition of NaCl on Spherical Ag Nanoparticles. Spherical Ag nanoparticles were prepared without the addition of NaCl . 20 mL EG solution containing 46.5 mM AgNO_3 and 264 mM PVP in a 100 mL three-necked flask was heated from

room temperature to 198 °C in an oil bath. After cooling the solution down to room temperature, 0.6 mL of NaCl (10 mM in EG) was added. The concentration of NaCl was 0.3 mM. Then the solution was heated to 198 °C.

Effect of Addition Temperature of NaCl on Reagent Solution. First, 17.4 mL EG solution containing 0.586 g PVP (MW: 40000) and 2 mL AgNO_3 solution (0.465 M in EG) were placed in a 100 mL three-necked flask. Then the mixture was heated from room temperature in an oil bath. During the heating process, 0.6 mL NaCl solution (0.01 M in EG) was added to the mixture at different temperatures. The concentrations of AgNO_3 , NaCl , and PVP in EG were 46.5, 0.3, and 264 mM, respectively. The reaction system was then cooled naturally to room temperature after reaching the boiling point of EG (198 °C). The reacting solution experienced a series of color changes before the color became stable.

Characterization. Morphologies of the Ag nanoparticles were observed using transmission electron microscopy (TEM; JEOL JEM-2010 at 200 kV). Product solutions were centrifuged at 12000 rpm three times for 30 min to ensure complete collection of the products each time. The precipitates were collected then re-dispersed in ethanol. Samples for TEM measurements were prepared by placing a droplet of the colloidal solutions on the carbon-coated grids. Ultraviolet/visible (UV–vis) extinction spectra were obtained (UV-3600; Shimadzu Corp.) using a quartz cell. The sample solution was diluted with EG. Aliquots of the solution were taken separately at various temperatures in the course of one reaction using glass pipettes when the reaction was monitored by UV–vis spectra. The original solutions used for UV–vis extinction spectra detection were diluted by a factor of 100 with an EG solvent.

Results and Discussion

Effect of NaCl Concentration. Ag nanostructures were prepared at various NaCl concentrations from 0 to 0.45 mM.

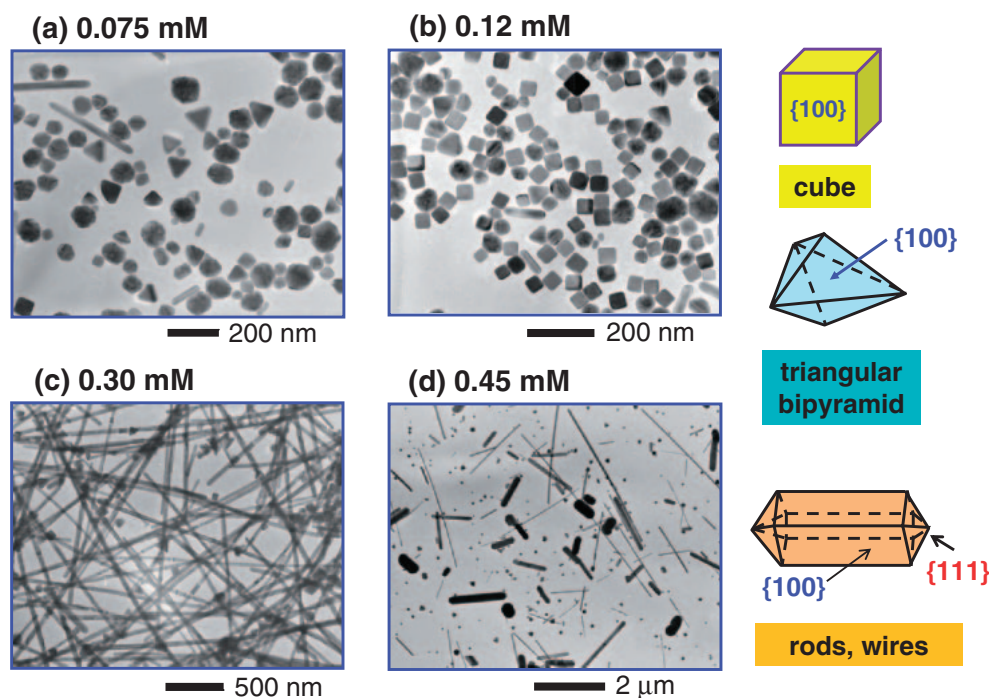


Figure 1. Typical TEM images obtained at 198 °C at various concentrations of NaCl : (a) 0.075, (b) 0.12, (c) 0.30, and (d) 0.45 mM.

When the Ag nanostructures were prepared without addition of NaCl, spherical particles with diameters of 20–100 nm were obtained, as will be shown in “Effect of addition of NaCl to spherical Ag nanoparticles.” Figures 1a–1d show TEM images of the products obtained at NaCl concentrations of 0.075, 0.12, 0.30, and 0.45 mM, respectively, where cubes, triangular bipyramids, one-dimensional (1-D) rods/wires, and quasi-spherical particles are produced. Based on TEM observations from various view angles and their selected area electron diffraction patterns, as reported previously,^{5c–5e} cubes, bipyramids, and nanowires have the crystal structures presented in Figure 1. Yields and average sizes of each Ag nanostructure at various NaCl concentrations are presented in Tables 1 and 2. At a low NaCl concentration of 0.075 mM, although products were mainly composed of spherical particles (65%) with diameters of 85 ± 26 nm, small amounts of cubes (18%), bipyramids (11%), and short rods (6%) were obtained. Some of the cubes, bipyramids, and short rods do not have sharp edges. It could be attributed to an extreme low NaCl concentration so that few AgCl nanoseeds were supplied for the further growth of well crystalline structures and slow oxidative etching by O_2/Cl^- . At the NaCl concentration of 0.12 mM, significant change in the product shapes occurred. Major products were cubes (61%) with average diameters of 46 ± 8 nm and quasi-spherical particles (30%) with average sizes of 68 ± 19 nm. At the NaCl concentration of 0.30 mM, the yield of cubes greatly decreased to 8% and 1-D products with diameters of 37 ± 8 nm and lengths of 3–24 μm became major products (75%). At the highest NaCl concentration of 0.45 mM, the yield of 1-D products decreased to 47%. But the diameters of the 1-D products increased to 100 ± 60 nm with shortening of their lengths (0.3–3 μm). On the basis of these observations, obviously, the addition of different amounts of NaCl could tune morphologies and sizes of the final products from spheres via cubes to 1-D rods/wires. We have found that the NaCl concentration of 0.12 mM could be the best for the synthesis of

the Ag cubes, 0.30 mM for the preparation of the monodispersed 1-D products, and 0.45 mM for the formation of the 1-D products with larger diameters.

Figure 2 shows the UV–vis spectra of product solutions at 198 °C at various NaCl concentrations. As well-known, Ag nanostructures with different shapes and sizes exhibit different surface plasmon resonance (SPR) bands.^{1,5–10} The UV–vis spectrum of the product solution prepared without addition of NaCl shows a typical symmetric SPR band with a peak at 436 nm. This peak can be attributed to the extinction of spherical particles. When 0.075 mM of NaCl was added, the SPR band becomes broad with a flat peak in the region of 400–500 nm. This peak arises from overlap of SPR bands resulting from spherical particles, cubes, bipyramids, and nanorods of various sizes. When the concentration of NaCl increased to 0.12 mM, a sharp and strong SPR band with a peak at 466 nm appears. This peak can be assigned to SPR band of the Ag cubes with an average diameter of ca. 50 nm. At a relatively high NaCl concentration of 0.30 mM, the strongest SPR peak at 395 nm and a weak shoulder peak at 355 nm occur. These peaks are assigned to two different transversal modes of the 1-D products with a pentagonal cross section, corresponding respectively to the out-of-plane dipole resonance and out-of-plane quadrupole resonance modes.^{10c,10d} Another weaker shoulder peak with a long tail band above 450 nm can be ascribed to the overlapping of the in-plane quadrupole and dipole resonance modes of the Ag nanowires with the peaks at 445 and 514 nm, respectively.^{10d} When the NaCl concentration

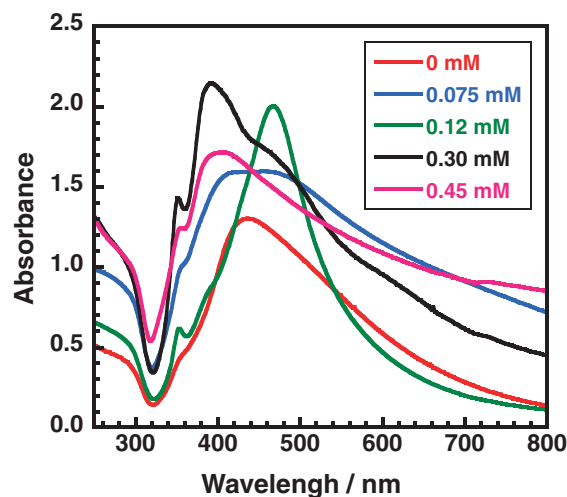


Figure 2. UV–vis spectra of the reaction solution at NaCl concentration of 0, 0.075, 0.12, 0.30, and 0.45 mM.

Table 1. The Yield of Each Product (%) Obtained by Heating AgNO_3 (46.5 mM)/NaCl/PVP (264 mM)/EG Solutions to 198 °C at Different NaCl Concentrations

Concentration of NaCl/mM	Cubes	Triangular bipyramids	Rods and wires	Quasi-spheres
0.075	18	11	6	65
0.12	61	6	3	30
0.30	8	10	75	7
0.45	10	18	47	25

Table 2. Average Sizes of Each Product Obtained by Heating AgNO_3 (46.5 mM)/NaCl/PVP (264 mM)/EG Solutions to 198 °C at Different NaCl Concentrations

Concentration of NaCl/mM	Edge length/nm		Rods and wires		Quasi-spheres
	Cubes	Triangular bipyramids	Diameter/nm	Length/ μm	Diameter/nm
0.075	49 ± 11	74 ± 22	27 ± 8	0.08–0.45	85 ± 26
0.12	46 ± 8	52 ± 6	30 ± 3	0.2–1.5	68 ± 19
0.30	50 ± 14	105 ± 19	37 ± 8	3–24	77 ± 12
0.45	74 ± 20	66 ± 10	100 ± 60	0.3–3	51 ± 9

was increased to 0.45 mM, the UV-vis extinction has peaks at 355 and 403 nm and a broad tail band in the longer wavelength region above 400 nm. This indicates that the products included a large number of nanorods with larger diameters.

Effect of Temperature at a Constant NaCl Concentration. Based on the findings described above, we believe that the shape evolution of Ag nanostructures depends strongly on the concentration of Cl^- . Further experiments were carried out to examine the effect of temperature on the final products. Keeping the concentration of NaCl at a constant value of 0.30 mM, the Ag nanostructures were synthesized at lower temperatures of 120 and 148 °C. Original reaction solutions were heated from room temperature to 120 °C and kept at this temperature for 2.5 h or heated to 148 °C and kept at this temperature for 1 h. Since the reduction rate of Ag^+ at 120 °C is much slower than that at 148 °C, a longer heating time is necessary to complete the reduction of Ag^+ ions. Yield and average size of each product are given in Tables 3 and 4. For comparison, the corresponding Ag products synthesized at 198 °C are also present. In this case, the reaction was stopped just after the solution was heated from room temperature to 198 °C for about 20 min.

Figure 3a depicts a typical TEM image of the Ag nanoparticles obtained under oil-bath heating at 120 °C for 2.5 h. Major products were nanorods (57%) with an average diameter of 39 ± 21 nm and length range of 0.4–3.5 μm . Among them, bipyramids with an average size of 116 ± 35 nm take a relatively high yield (31%) and the yield of cubes is only 2%. Figure 3b presents a typical TEM image obtained at 148 °C. The yield of 1-D nanostructures increases to 68%, whereas that of the bipyramids decreases to 18% and the yield of cubes remains low (3%). We have synthesized 1-D Ag products in a high yield (75%) at 198 °C. These findings suggest that keeping the reaction solution at low temperatures such as 120

Table 3. The Yields of Each Product (%) Obtained by Heating AgNO_3 (46.5 mM)/NaCl (0.3 mM)/PVP (264 mM)/EG Solutions to Different Temperatures

Temperature /°C	Cubes	Triangular bipyramids	Rods and wires	Quasi-spheres
120	2	31	57	10
148	3	18	68	11
198	8	10	75	7

Table 4. Average Sizes of Each Product Obtained by Heating AgNO_3 (46.5 mM)/NaCl (0.3 mM)/PVP (264 mM)/EG Solutions to Different Temperatures

Temperature /°C	Edge length/nm		Rods and wires		Quasi-spheres
	Cubes	Triangular bipyramids	Diameter/nm	Length/ μm	Diameter/nm
120	66 ± 7	116 ± 35	39 ± 21	0.4–3.5	37 ± 17
148	79 ± 12	135 ± 45	42 ± 23	0.3–3.7	72 ± 24
198	50 ± 14	105 ± 19	37 ± 8	3–24	77 ± 12

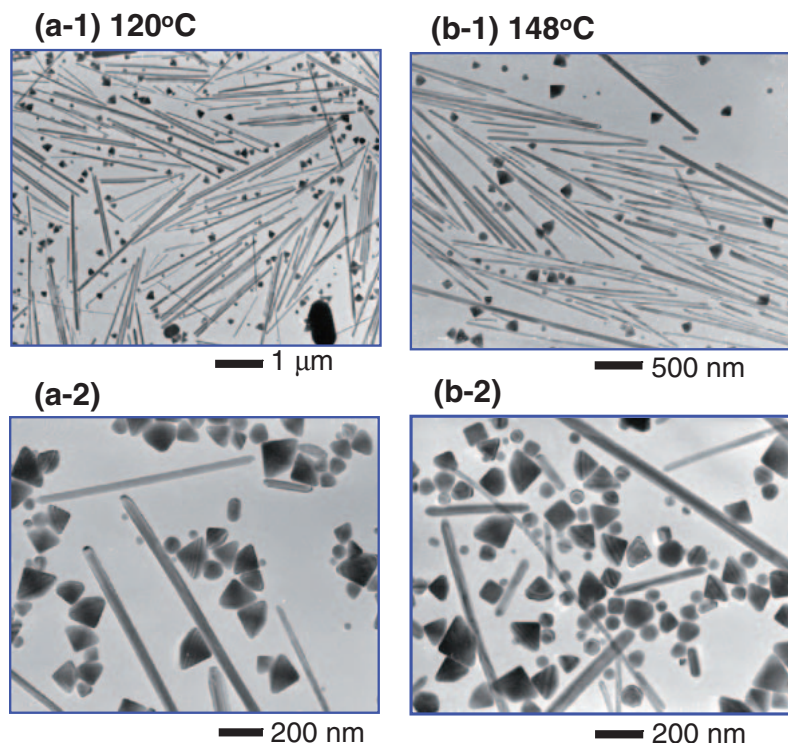


Figure 3. Typical TEM images of Ag nanoparticles obtained at (a) 120 and (b) 148 °C.

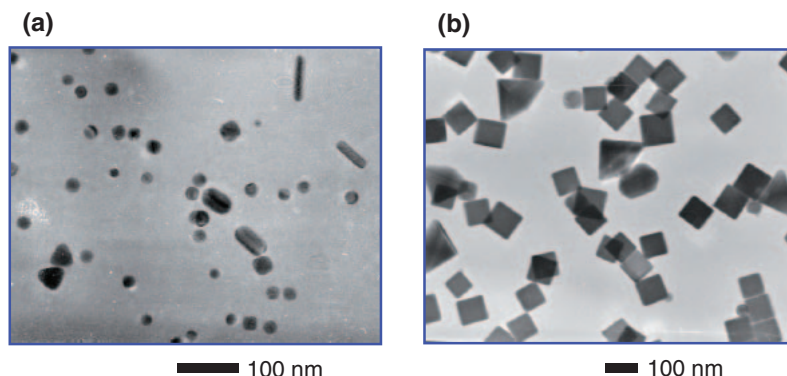


Figure 4. Typical TEM image of Ag nanostructures obtained from (a) AgNO_3 (0.3 mM)/ NaCl (0.3 mM)/PVP (264 mM)/EG system and (b) addition of 1 mL of AgNO_3 (0.93 M) at 185 °C to the same solution as that used in experiment (a) and heated for 1 h.

and 148 °C will be favorable to the production of single-twin triangular bipyramids, while yields of single crystal cubes and 1-D products become lower. No significant differences were observed in average sizes between the cubes and bipyramids prepared at 120 and 148 °C and those obtained at 198 °C. Although average diameters of the 1-D products obtained at 120 and 148 °C are similar to that obtained at 198 °C (ca. 40 nm), lengths of the 1-D products obtained in the lower temperatures (0.3–3.7 μm) are shorter than that at 198 °C (3–24 μm) by about one order of magnitude.

The growth process of the Ag nanostructures was monitored by UV–vis spectra (Figures S1a and S1b in Supporting Information). UV–vis spectra of the Ag nanoparticles prepared at 120 °C (Figure S1a) present a symmetric SPR band with a peak maximum at ca. 410 nm due to the appearance of smaller Ag seeds. The peak intensity increases after heating for 25 min. After heating for 80 min, two weaker peaks of Ag nanorods appear at 350 and 390 nm and a stronger peak of cubes and bipyramids is observed at 440 nm. The SPR peaks of the 1-D products become distinguished, whereas that of the cubes and bipyramids becomes weak, when heating time reaches 100 min. After that, the intensities of SPR peaks of 1-D products enhance continuously but peak positions are nearly unchanged at 2.5 h. Because the UV–vis spectrum for the 1-D Ag nanostructures is significantly stronger than those for other shaped particles such as cubes and bipyramids, the extinction peaks for the Ag cubes and bipyramids are submerged when their yields are less.

Evolution of the SPR bands with reaction time at 148 °C is very similar to that at 120 °C though the reduction rate is much faster at the higher temperature (Figure S1b). A very weak SPR band appears at 100 °C, and an obvious symmetric peak for the Ag seeds is observed at 148 °C. SPR bands observed after heating for 8, 10, 17, and 60 min at 148 °C are similar to those after heating for 80, 100, 120, and 180 min at 120 °C. These findings are consistent with TEM image observations of the Ag products where no significant differences are found for the distributions and sizes of final products between 120 and 148 °C.

Effect of Addition of NaCl to Spherical Ag Nanoparticles. An important effect of the addition of NaCl is shape selective oxidative etching by O_2/Cl^- .^{1,5f,6} Here, O_2 gas can dissolve in EG. We examined whether large spherical Ag particles can be etched by O_2/Cl^- and changed into anisotropic

particles. Initially, large spherical particles with the diameter range in 20–100 nm were prepared under heating at 198 °C without addition of NaCl in the original solution. Then, NaCl solution was added to the original solution. The final concentration of NaCl in the mixture was 0.3 mM, which was the same concentration as that used for the preparation of the 1-D Ag nanowires in high yield. The mixture was heated again to 198 °C for about 20 min. To examine the shape transition of the spherical Ag particles, UV–vis spectra of the reaction solution were measured at various temperatures (Figure S2a in Supporting Information). The UV–vis data indicate little changes in peak intensity and band width of the typical symmetric SPR band for the spherical Ag nanoparticles. This implies that the shapes and sizes of the Ag spherical particles are not significantly influenced by the addition of NaCl at 198 °C.

Figure S2b (Supporting Information) shows the TEM image of the final product obtained at 198 °C. All of the particles are still spherical and little anisotropic product is obtained. The TEM observation suggests that it is difficult to etch larger spherical Ag particles by Cl^-/O_2 . Apparently, the shape transition of the Ag particles from spherical to anisotropic crystals does not occur once the larger spherical particles are formed. This is also consistent with little change in UV–vis spectra of the above reaction solution containing the spherical Ag particles by the addition of NaCl at 198 °C. The contrast study reveals that the presence of Cl^- ions at the early stage before the formation of the large Ag particles could be important for the formation of the anisotropic Ag nanostructures.

Effect of AgCl for the Formation of Anisotropic Ag Nanostructures. An important role of the addition of NaCl at low temperature may be the initial formation of AgCl , which acts as seeds for the formation of anisotropic Ag nanostructures. Since the solubility constant of AgCl in EG is expected to be very low at room temperature, almost all Cl^- in NaCl can be converted to AgCl when 0.3 mM AgNO_3 and 0.3 mM NaCl were premixed at room temperature. When the solution was heated to 198 °C, cubes and bipyramids with less sharp edges were obtained (Figure 4a). However, when new AgNO_3 solution was added to the solution at 185 °C dropwise, and subsequently the whole reaction system was heated to 198 °C and kept at this temperature for 1 h, mixtures of Ag cubes and bipyramids with sharp edges were obtained (Figure 4b). These results indicate that the nanoparticles

produced at the first step become seeds for overgrowth of the cubes and bipyramids. There are few 1-D products grown from these seeds. Since Cl^-/O_2 (dissolved in EG) can etch cubes and bipyramids,^{5f} quasi-spherical particles were observed under our experiment conditions. An important finding in this section is that AgCl seeds prepared at room temperature can be converted to cubes and bipyramids during heating from room temperature to 198 °C. However, the transition from AgCl seeds to 1-D products via decahedrons does not happen.

Effect of Addition Temperature of NaCl to Reaction Solution. We have shown that the concentration of NaCl in the initial solution is an important factor for the preparation of anisotropic Ag nanostructures. In the previous section, we have also demonstrated that AgCl nanoparticles formed at low temperature can act as precursors of the produced Ag nanoparticles with well-defined shapes. To further understand the effect of NaCl, we have performed a series of experiments by adding NaCl to the original solution at different reaction temperatures (80, 120, 154, 160, 170, and 198 °C) and heating the solution to 198 °C or keeping it at 198 °C when NaCl was added at 198 °C. The change of the reaction solution with temperature has been continuously traced by observing UV–vis spectra. We have found that no SPR peak appears below 90 °C (not shown in Figure 5), indicating that the reduction of Ag^+ ions and the nucleation of Ag nanoparticles do not happen at this low temperature because EG molecules decompose at the temperature above ca. 90 °C on the basis of TG measurement of pure EG. In Figure 5, a weak symmetric SPR peak at ca. 410 nm appears at 120 °C due to the formation of small Ag seeds. With the increase of the solution temperature from 154 to 198 °C, the SPR band gradually becomes stronger and wider due to the continual growth of the spherical Ag particles. Assuming that the intensity of the SPR peak is proportional to amount of formed metallic Ag, we estimate that about 20, 50, 90, and 100% of the total amount of AgNO_3 could be reduced and converted into Ag nanoparticles at 120, 154, 160, 170, and 198 °C, respectively.

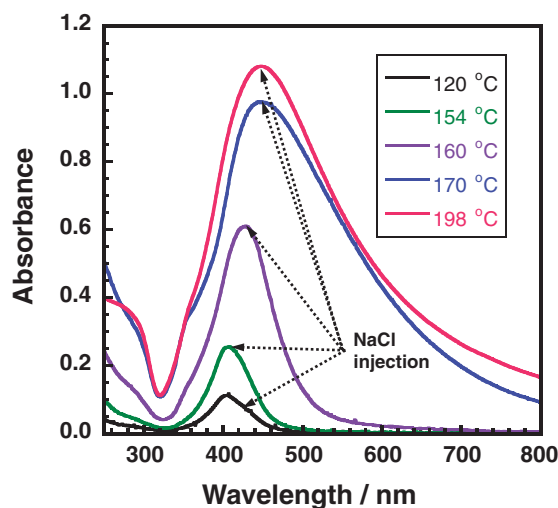


Figure 5. UV–vis spectra of Ag nanoparticles when $\text{AgNO}_3/\text{PVP}/\text{EG}$ solution was heated from room temperature (20 °C) to 198 °C.

TEM images (not shown here) of the final products obtained by injecting NaCl at 80 °C show little difference in comparison to those obtained by the injection of NaCl at room temperature (20 °C), shown in Figure 1c. This implies that the injection of NaCl before nucleation starts has little effect on the shapes and sizes of final products. Figures 6a–6d show TEM images of the final products obtained by the addition of NaCl when reaction solution temperature reaches 120, 154, 160, and 170 °C, respectively. Distributions of each product and their average sizes are listed in Tables 5 and 6. Results obtained by injecting NaCl at 198 °C (not shown here) are essentially identical with those produced at 170 °C. With the increase in the injection temperature of NaCl from 20 to 170 °C, the yield of 1-D products decreases from 75 to 1%, whereas that of spherical Ag particles increases from 7 to 99%. Yields of the Ag cubes and bipyramids increase from about 10 to 20% with the temperature change from 20 to 120 °C, and then they decrease to zero when increasing the addition temperature from 120 to 170 °C. Average sizes of the Ag cubes and bipyramids decrease from 50 ± 14 and 105 ± 19 nm to 37 ± 5 and 49 ± 11 nm, respectively, with increasing the addition temperature from 20 to 160 °C. The length of 1-D products becomes much shorter from 3–24 to 0.08–0.1 μm with increasing the addition temperature from 20 to 170 °C.

Figures S3a–S3d (Supporting Information) show the UV–vis spectra measured from the solutions sampled at various temperatures. In all cases, before injection of NaCl, a symmetric SPR band with a peak at ca. 410 nm appears at ca. 100 °C and becomes stronger and broader with the increase of the reaction solution temperature. The shapes and wavelengths of SPR bands depend on the injection temperature of NaCl. The extinction spectra obtained by the injection of NaCl at 120 °C give peaks A and B related to 1-D products and weak peak C related to cubes and bipyramids. With the increase in the injection temperature of NaCl, peaks A and B become less prominent and a symmetric SPR peak D related to quasi-spherical particles becomes prominent. When NaCl was added at 160 and 170 °C, peaks A and B become weak or disappear and broad SPR peaks D related to spherical particles are strongly observed. These observations are consistent with the observations from TEM images of final products.

The most important finding in this session is as follows. To obtain anisotropic Ag nanoparticles in high yields, injection of NaCl at low temperature is required. This indicates that Cl^- plays an important role just at nucleation and initial crystal growth stages. It is difficult to transfer spherical particles into anisotropic particles by Cl^-/O_2 oxidative etching at high temperatures with the injection of NaCl. The concentration of AgCl decreases when increasing the injection temperature because the solubility constant of AgCl in EG increases with the increase in the solution temperature. We have found that AgCl also is an important precursor for the formation of cubes and bipyramids. The decrease in yields of cubes and bipyramids with the increase of injection temperature of NaCl might be due to the decrease in the concentration of AgCl at higher injection temperatures.

Formation Mechanism of Ag Nanostructures. From the present experiments, we have distinctly revealed that morphologies of the final products are related to various experimental

parameters such as the concentration of NaCl, temperature of reaction solution, and the injection temperature of NaCl. There are three possible roles played by NaCl. The first is the formation of AgCl, which may become seeds of anisotropic Ag nanostructures. The second is that Cl^- ions act as adsorbers.

Table 5. The Yield of Each Product (%) Obtained by Heating AgNO_3 (46.5 mM)/NaCl (0.3 mM)/PVP (264 mM)/EG Solutions to 198 °C at Different Injection Temperatures of NaCl

Injection temperature/°C	Cubes	Triangular bipyramids	Rods and wires	Quasi-spheres
20	8	10	75	7
120	21	20	43	16
154	8	12	31	49
160	5	11	19	65
170	0	0	1	99

Cl^- anions can more easily adsorb on {100}-type facets of the Ag particles so that the {100}-facet-dominated Ag nanocrystals are preferentially produced. The third is that Cl^- ions can also act as an etchant in the presence of O_2 in EG. The first effect is especially important at low temperature, where the solubility constant of AgCl is very low. Once increasing solution temperature AgCl is slowly dissolved and decomposed into Ag^+ and Cl^- in EG. Ag^+ ions are further reduced into elemental Ag^0 . In general, shapes of the final products depend not only on the stability of crystal structures against etching by Cl^-/O_2 but also the density of Ag^0 atoms around the growing nuclei. A high related ion concentration around the nuclei can create an environment with high twinning probability for the formation of such twinned particles as twin-plates and five-twinned decahedra from which pentagonal 1-D rods and wires are grown. Thus, five-twinned 1-D products are favorable at higher concentration of Ag^+ ions, whereas single crystal cubes are preferentially formed at lower concentration of Ag^+ ions.

Table 6. Average Sizes of Each Product Obtained by Heating AgNO_3 (46.5 mM)/NaCl (0.3 mM)/PVP (264 mM)/EG Solutions to 198 °C at Different Injection Temperatures of NaCl

Injection temperature/°C	Edge length/nm		Rods and wires		Quasi-spheres
	Cubes	Triangular bipyramids	Diameter/nm	Length/ μm	Diameter/nm
20	50 $\pm$ 14	105 $\pm$ 19	37 $\pm$ 8	3–24	77 $\pm$ 12
120	46 $\pm$ 11	73 $\pm$ 9	38 $\pm$ 8	0.3–0.2	50 $\pm$ 27
154	43 $\pm$ 4	72 $\pm$ 18	22 $\pm$ 7	0.1–2	54 $\pm$ 22
160	37 $\pm$ 5	49 $\pm$ 11	23 $\pm$ 10	0.1–0.4	97 $\pm$ 49
170			51 $\pm$ 6	0.08–0.1	47 $\pm$ 15

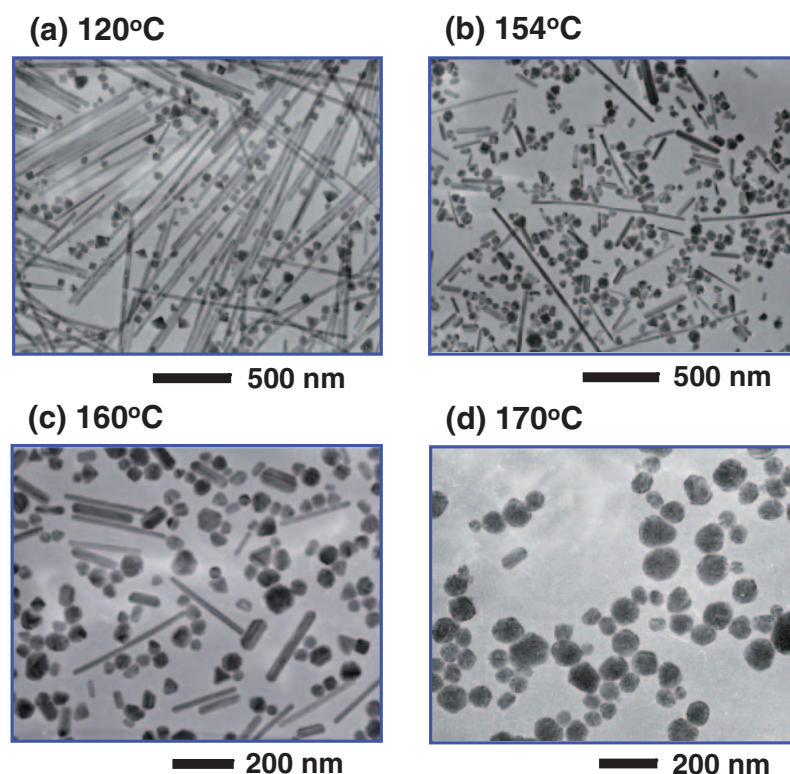
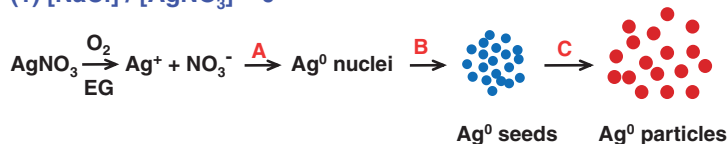
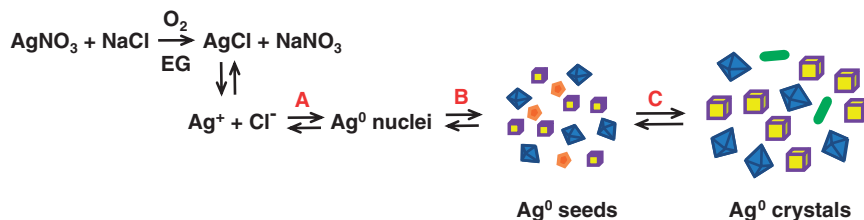


Figure 6. Typical TEM images of as-synthesized Ag nanostructures by injection of NaCl into reaction solution at (a) 120, (b) 154, (c) 160, and (d) 170 °C.

(1) $[\text{NaCl}] / [\text{AgNO}_3] = 0$ (2) $[\text{NaCl}] / [\text{AgNO}_3] = 1$ (3) $[\text{NaCl}] / [\text{AgNO}_3] = 0.0065$ 

Scheme 1. Possible nucleation and growth mechanisms of Ag nanostructures at different molar ratios of $[\text{NaCl}]/[\text{AgNO}_3]$.

On the basis of our present study, mechanisms for the formation of Ag nanostructures can be classified into three cases as shown in Scheme 1, depending on the molar ratios of $[\text{NaCl}]/[\text{AgNO}_3]$. Case (1) is $[\text{NaCl}]/[\text{AgNO}_3] = 0$. Without the addition of NaCl, Ag^+ ions are reduced to Ag^0 , nucleation occurs, and then the Ag seeds are formed and their growth leads to spherical particles formed randomly. Case (2) is $[\text{NaCl}]/[\text{AgNO}_3] = 1$. When equal molar concentrations of AgNO_3 and NaCl were mixed at room temperature, AgCl is formed because of the small solubility constant of AgCl. In this case, AgCl is dissolved as Ag^+ and Cl^- with increasing temperature. After then Ag^+ ions are reduced to Ag^0 and nucleation, seed formation, and crystal growth take place. Since the concentration of Ag^+ ions is low, twinning probability is low. Therefore, single crystal cubes and single-twin bipyramids are produced preferentially. Case (3) is an intermediate between the above two cases: $[\text{NaCl}]/[\text{AgNO}_3] = 0.0065$. In this case although AgCl is formed, a large excess amount of AgNO_3 is present in the solution. The standard electrode potential of $\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$ (+0.2233 V vs. SHE) is lower than that of $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ (+0.799 V vs. SHE). Under such conditions, most of the Ag^0 atoms do not arise from AgCl but from free Ag^+ . In this case, major products are five-twinned 1-D particles because the concentration of Ag^+ ions is sufficient to provide a high probability for twinning.

Although the real role of Cl^- anions leading to different anisotropic Ag nanostructures in each condition is still unclear, the injection of NaCl at different temperature provides some information about whether O_2/Cl^- etching is significant or not for the formation of anisotropic Ag nanostructures under the present conditions. We injected NaCl at solution temperatures

of 80, 120, 154, 160, 170, or 198 °C where the reaction stage is different. At 80 °C, the reduction does not start (A in Scheme 1). At 120 °C, just small seeds start to produce (B in Scheme 1), while at 154 and 160 °C, Ag seeds become larger (C in Scheme 1). The reduction reaction nearly finishes at 170 °C and completely finished at 198 °C. We have found that the yield of spherical particles increases from 7 to 16% when the injection temperature of NaCl increases from 20 to 120 °C. This implies that complete re-dissolution of spherical seeds to Ag^+ and re-reduction leading to anisotropic Ag nanostructures does not occur even when NaCl was added to the solution just after the production of small Ag seeds. Thus, we conclude that major roles of NaCl have two points in our study. One is to form AgCl seeds at lower temperatures and another is to act as adsorbers to selectively stabilize {100} facets during crystal growth.

We have also found that the concentration of NaCl strongly affects the final shapes of products. Cubes are produced preferentially at the NaCl concentration of 0.12 mM, whereas 1-D products are major products at the NaCl concentration of 0.30 mM. In our previous experiments under bubbling O_2 ,^{5f} we found that cubes and bipyramids are etched by Cl^-/O_2 , whereas decahedrons can survive Cl^-/O_2 etching and grow into 1-D rods or wires under certain conditions. Thus, one reason for the favorable formation of the cubes at lower NaCl concentration may be explained in terms of a slower etching of the cube seeds due to the low NaCl concentration.

When AgNO_3 was reduced at 120 and 154 °C at the NaCl concentration of 0.30 mM, major products were the 1-D products and bipyramids and little cubes could be prepared.

Under these conditions, seeds of cubes are either difficult to be formed or their etch rates by O_2/Cl^- are faster than those of the bipyramids and 1-D products.

We have demonstrated that the final Ag products depend on the injection temperature of NaCl. If NaCl was injected into the solution at a low temperature, most of the Cl^- ions exist as AgCl nuclei because the solubility constant of AgCl in EG is very small at low temperature. The AgCl particles first nucleate and then serve as the seeds for the growth of Ag nanocrystals. On the contrary, because the solubility constant of AgCl enhanced rapidly at high temperature, some AgCl nuclei dissolve in EG solution. In addition, the standard electrode potential of Ag^+ is higher than AgCl. It means that Ag^+ ions can be reduced into Ag atoms much easier than AgCl. Usually without the introduction of NaCl, the reduction process was finished at a relatively low temperature. Therefore, when we injected NaCl into the solution including AgNO_3 beyond 170°C , most of the Ag^+ ions have been reduced and large spherical particles cannot be etched by Cl^-/O_2 . Under such conditions, Cl^- ions have little effect on the final Ag particle morphologies. This leads to the final products dominated by quasi-spherical particles.

Conclusion

Various Ag nanostructures have been prepared by reducing AgNO_3 in EG in the presence of PVP and NaCl. Different experimental parameters such as the concentration of NaCl, the solution temperature, and the injection temperature of NaCl have been modified to examine the effects of addition of NaCl on the obtained product morphologies. At the NaCl concentration of 0.12 mM, Ag cubes have a higher yield of 61% while Ag nanowires dominate in the products at the NaCl concentration of 0.3 mM. Reaction temperature decides the reduction power and only nanorods, cubes, and bipyramids were produced at relatively low temperatures. We have observed that the larger spherical Ag particles are difficult to be etched. Furthermore, we have also found that the temperature of adding NaCl into the reaction solution can control the formation of the Ag nanowires. Changing the solution temperature at which NaCl is introduced into the solution can effectively influence the yields of different Ag structures by adjusting the ratios of Ag and AgCl seeds formed in the solution. This work provides a significant insight into the roles of Cl^- in the crystal growth of various Ag nanostructures. Various experimental parameters examined here give some new information on optimum experimental conditions for the preparation of various anisotropic Ag nanostructures by the polyol reduction method.

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Supporting Information

TEM images and UV–vis spectra of Ag nanostructures prepared from $\text{AgNO}_3/\text{PVP}/\text{EG}$ and $\text{AgNO}_3/\text{NaCl}/\text{PVP}/\text{EG}$ mixtures at various conditions. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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