Growth Process of Ag Triangular Nanoplates Observed by In Situ XAFS

H Murayama, N Hashimoto and H Tanaka
Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 13-27 Kasuga Bunkyo-ku 112-8551 Tokyo JAPAN
E-mail: htanaka@kc.chuo-u.ac.jp

Abstract. We examined to establish the simple synthesis method of Ag triangular nanoplates in order to elucidate their growth process. Ethanol solution of AgNO₃ was photoirradiated without reduction agents except in the presence of PVP, polyvinylpyrrolidone). Electron microscope observations revealed that the shape of the product was Ag triangular nanoplates with sharp corners and a flat face. In situ XAFS and optical absorption measurements suggested that the Ag triangular nanoplates were photoinduced-converted from Ag spherical nanoparticles via Ag truncated triangular nanoplates.

1. Introduction
Anisotropic nanocrystals have attracted much attention because of their unique properties depending on their shapes. Especially, Ag triangular nanoplates are one of the most desired anisotropic nanocrystals in the fields of catalysts and optical devices [1]. In fact, several synthesis methods and their growth processes have been proposed. For example, Mirkin et al. successfully synthesized the Ag triangular nanoplates by the photoinduced aggregation method using the combination of trisodium citrate dihydrate and NaBH₄ as reduction agents in the presence of BSPP. They proposed photoinduced conversion of Ag nanospheres to nanoplates driven by Ag redox cycles [2]. On the other hand, Brus et al. successfully synthesized the Ag triangular nanoplates by the photoinduced growth method using the same reduction agents in the presence of additional Ag ions. They proposed surface plasmon enhanced photoreduction of Ag ions adsorbed on preformed Ag seeds [3]. Since the proposed growth processes in these reports seem to be strongly related to the synthesis methods using a lot of agents, establishment of the more simple synthesis method has been desired in order to elucidate the growth process.

In this study we examined newly synthesis method of the Ag triangular nanoplates by photoirradiation to AgNO₃ ethanol solution without reduction agents except in the presence of poly(vinyl-pyrrolidone) (PVP) under the anaerobic condition. The shapes and crystal structures of the products were observed by STEM images. The local coordination structures were analyzed by using the in situ Ag K-edge XAFS data. The optical properties related to the shapes of Ag nanostructures were monitored by UV-vis spectra. The growth process of the Ag triangular nanoplates was discussed based on the photoinduced conversion of Ag spherical nanoparticles.
2. Experimental

AgNO₃ powder and PVP (K = 30, Mw = 40 000) were dissolved in 5 mL and 20 mL of ethanol, respectively. These solutions were mixed together in a glass vial while the total volume of the mixed solution was adjusted to 30 mL by dilution with ethanol. The mixed solution thus prepared was degassed by applying a freeze-pump-thaw method as four cycles, and subsequently was irradiated by a 500 W high-pressure Hg lamp. The obtained solution was deposited on a collodion-coated copper grid for microscopic observation. Bright-field STEM and SEM images for the specimen were observed by a field emission type SEM (S-5500, HITACHI) operated at 30 kV. High resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were also observed by a LaB₆ high-resolution TEM (H-9500, HITACHI) operated at 300 kV.

On the other hand, the mixed solution was placed in a PMMA cell with an optical path length of 50 mm for XAFS measurements during the synthesis. The Ag K-edge XAFS spectra were collected at NW10A station, PF-AR (IMSS, KEK, Tsukuba, Japan) equipped with a Si(311) double crystal monochromator in a transmission mode used by two ionization chambers filled with Ar gas for incident intensity and Kr gas for transmitted intensity, respectively. The XAFS spectra were analyzed by the program package REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) was extended from an EXAFS oscillations observed for Ag foil.

3. Results and discussion

3.1. Shape and crystal structure

Figure 1(a) shows the STEM image of final products obtained with photoirradiation time at 18 h. Ag triangular nanoplates with sharp corners are observed dominantly and their typical edge length is ~ 50 nm. The SEM image shown in the inset also supports that the shape of the product is a Ag triangular nanoplate with a flat face. In addition, a tilted SEM image revealed that their thickness was estimated as ~ 10 nm. An HRTEM image showed that the products were composed of fcc Ag metal because of the observation of lattice fringes at a spacing of ~ 0.25 nm. An SAED pattern recorded by the electron beam directed perpendicular to a triangular face of the Ag triangular nanoplate showed that their flat faces were presented by {111} planes because of the observation of diffraction spots with the 6-fold rotational symmetry. The Ag triangular nanoplates were found to be successfully synthesized by this present method, which is simple photoirradiation to the mixed ethanol solution of AgNO₃ and PVP.

Figure 1(b) and (c) show the STEM images of typical products obtained with photoirradiation time at 5 h and 7 h, respectively. At 5 h, spherical nanoparticles of which diameter is less than 10 nm are observed. On the other hand, at 7 h, truncated triangular nanoplates of which edge length is ~ 40 nm are observed.

Figure 1. STEM images of the products obtained with photoirradiation time at 5 – 18 h. The inset in panel (a) shows the SEM image for the Ag triangular nanoplate. Scale bar is 50 nm.
start to be observed while the small spherical nanoparticles are still observed. These results suggest that the Ag triangular nanoplates are formed by photoinduced conversion of the small Ag spherical nanoparticles.

3.2. Local coordination structure

Figure 2 shows Fourier-transformed spectra of the $k^3$ weighted Ag K-edge EXAFS oscillations collected during the photoirradiation. In all the photoirradiation time, the highest peak is distributed in the range of 0.23 − 0.31 nm. This peak can be assigned to the scattering from the first nearest-neighbor Ag atoms because the peak profile was similar to that for the Ag foil. However, no peak due to Ag oxide and Ag ionic species, which predicted lower bond distance, is observed even at 4 h. These results indicate that the small metallic Ag nanoparticles are formed and that the reduction of Ag ions to Ag metals was completed before 4 h. Moreover, the peak due to the scattering from the 3rd neighbor Ag atoms is observed slightly in the range of 0.45 − 0.52 nm in the spectrum at 12 h, while the peaks are not observed at 4 h and 8 h. This supports the result that the Ag crystals are grown up with the photoirradiation time in the solution as described in section 3.1.

Table 1 shows summary of curve-fitting analysis of the data for the Ag triangular nanoplates. Coordination number, $N$, for Ag-Ag increases from 9 up to 12 as the photoirradiation time increases, while bond distance, $r$, for Ag-Ag keeps to be constant at 0.292 nm, of which bond distance is close to that of 0.289 nm for the Ag foil. It is noted that in all photoirradiation time, the energy difference, $dE$, is sufficiently small and the Debye-Waller factor, $\sigma$, is quite close to that for the Ag foil (0.006). Taking into consideration of completion of the reduction of the Ag ions before 4 h, the Ag triangular nanoplates were formed by the aggregation of the small spherical nanoparticles.

| photoirradiation time / h | coordination number | distance / nm | $dE$ / eV | $\sigma$ / nm |
|---------------------------|---------------------|---------------|----------------|---------------|
| 4                         | 9                   | 0.292         | 4.7            | 0.0095        |
| 8                         | 11                  | 0.292         | 6.8            | 0.0082        |
| 12                        | 12                  | 0.292         | 5.2            | 0.0083        |

\(^a\)energy difference in the absorption threshold between the model compounds and the triangular Ag nanoplates.  
\(^b\)Debye-Waller factor.  Ag-Ag bond for the Ag foil ($N = 12$, $r = 0.289$ nm, $dE = 0$, $\sigma = 0.006$) derived from the EXAFS spectrum as the references.
3.3. Optical property

Figure 3 shows UV-vis spectra of the colloidal solution measured during the photoirradiation. At 1 h, single absorption peak is observed at 410 nm. Once the peak at 410 nm increases at 2 h, this peak decreases as the photoirradiation time increases. On the other hand, a shoulder peak appears at ~500 nm at 4 h. Peak seems to be shifted toward 700 nm as the photoirradiation time increases. It is known that the peak at 410 nm is attributed to the surface plasmon resonance which is characteristic of the Ag spherical nanoparticles, and the absorptions at 500 nm and 700 nm are attributed to in-plane dipole plasmon resonance of truncated triangular nanoplates and sharp triangular nanoplates, respectively [4]. The continuous changes of these features indicate that the Ag triangular nanoplates were gradually formed from the Ag spherical nanoparticles via the Ag truncated triangular nanoplates.

Furthermore no reaction proceeded without the photoirradiation. Even when the photoirradiation was stopped in the middle of the reaction, the changes of the spectrum was interrupted immediately. These results indicate that photoirradiation is essentially necessary to proceed the formation of the Ag triangular nanoplates.

![Figure 3. UV-vis spectra for the mixed solution obtained with photoirradiation time at 0 – 12 h.](image)

4. Conclusion

The Ag triangular nanoplates were successfully synthesized from the mixed ethanol solution of AgNO₃ and PVP by photoirradiation under the anaerobic condition. The growth process is explained as follows: (1) the small Ag spherical nanoparticles were produced from photoinduced reduction of Ag ions, (2) the Ag triangular nanoplates were produced from the Ag spherical nanoparticles via the Ag truncated triangular nanoplates by photoirradiation.

Acknowledgement

We are grateful to the approval of the Photon Factory Advisory Committee (proposal No. 2007G700) at KEK for XAFS measurements. We thank Mr. Y. Tsubota at HITACHI High-Technologies for observation of HRTEM and SAED.

References

[1] Jin R, Cao Y W, Mirkin C A, Kelly K L, Schatz G C and Zheng J G 2001 *Science* **294** 1901
[2] Xue C, Metraux G S, Millstone J E and Mirkin C A 2008 *J. Am. Chem. Soc.* **130** 8337
[3] Maillard M, Huang P and Brus L 2003 *Nano Lett.* **3** 1611
[4] Chen S and Carroll D L 2002 *Nano Lett.* **2** 1003