

Hydrothermal Synthesis of Silver Nanoparticles

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Summary

The hydrothermal synthesis of Ag nanoparticles has been examined using the flow-type reactor for 40 MPa and for different temperatures and flow rates. Polyvinylpyrrolidone (PVP) was used as a protective agent as well as a reducing agent. For temperatures of 250 and 300 °C, small nanoparticles of less than 50 nm were mainly produced. Lowering flow rate at these temperatures yielded the preferential formation of nanoparticles with intermediate size between 20 – 100 nm. For 350 °C, we found the simultaneous formation of small nanoparticles of less than 30 nm and relatively large particles of more than 100 nm, while almost no nanoparticles between 30 – 100 nm were formed. We also conducted the hydrothermal treatments of Ag nanoparticles which were prepared in advance by photochemical method at ambient temperature and pressure. While noticeable change in the particle size was not observed for hydrothermal treatments at 250 and 300 °C, significant amount of Ag nanoparticles disappeared during treatments at 350 °C, suggesting the depression of the protective action of PVP and the dissolution of Ag nanoparticles in subcritical water. Based on these observations, the formation mechanism of Ag nanoparticles on the hydrothermal synthesis has been discussed.

1. Introduction

Noble metal nanoparticles possess the distinctive optical properties such as large non-linear optical susceptibility (Hache, 1988, p.783), surface enhanced Raman scattering (Moskovits, 1985, p.55) and so on. By virtue of these properties, they have been promising as materials for novel optical devices. Various preparation methods for noble metal nanoparticles have been proposed since a long time ago, e.g., the chemical reduction of metal ions in solutions (Turkevich, 1951, p.1861), γ -radiolysis of metal ions (Henglein, 1989, p.1861). From viewpoints of practical applications, a further improvement is required to realize the mass production of ultra-fine nanoparticles with exciting novel properties.

Hydrothermal techniques have been widely used in many chemical processes including materials processing, crystal growth and waste treatment (Adshiri, 1994). In recent years, techniques of hydrothermal synthesis have been further developed by the combined use of electrode reactions and crystallization. While there have been many applications of hydrothermal techniques in the preparation of metal oxide nanoparticles, only a few works have been reported to explore the hydrothermal synthesis of noble metal nanoparticles. Recently, Kimura and coworkers (2003, p.131) reported the hydrothermal synthesis of Pt or Rh nanoparticles by reducing Pt(IV) or Rh(III) ions in the presence of PVP. In this study, we have examined the hydrothermal synthesis of Ag nanoparticles using the flow-type reactor, which allowed the consecutive preparation of a large amount of colloidal solutions. It is shown that Ag⁺ ions are thermally reduced and Ag nanoparticles are formed in the presence of PVP. The size evolution of Ag nanoparticles previously produced by photochemical method at ambient temperature and pressure during the hydrothermal treatment has been also investigated at various temperatures to explore the contributing factors which determine the size distribution of Ag nanoparticles produced by the hydrothermal method.

2. Experimental section

PVP (MW = 360,000, Kishida Chemical Co.) and AgNO₃ (Wako Pure Chemical Industries) were used as received. Aqueous solutions of the mixture of AgNO₃ (3 mM) and PVP (3 wt%) were prepared using singly deionized and distilled water.

A flow-type high-pressure reactor made of Hastelloy (inner volume ~ 1 cm³) was used for hydrothermal synthesis. The detail of the reactor has been already described elsewhere (Amita, 2001, p.3605). In brief, the reactor was equipped with two sapphire windows, capable of in situ measurements of absorption spectra during the reaction. The optical path length is 1 cm. AgNO₃/PVP aqueous solutions were injected into the reactor by a HPLC pump (PU-1580, JASCO Co.) at three different flow rates (0.2, 0.5, 1.0 cm³min⁻¹) and pressure was kept at 40 MPa by a back-pressure regulator (SCF-get, JASCO Co.). Temperature was controlled using a thermocouple and a jacket-type heater surrounding the reactor with the accuracy of 1°C.

Absorption spectra of reacting solutions inside the reactor were recorded in situ by a spectrophotometer (V-560, JASCO Co.). Small drops of Ag colloidal solutions prepared were placed onto the copper mesh and dried at room temperature in air for transmission electron microscopy (TEM) observations. TEM images were obtained using a Hitachi H-7000 electron microscope operated at an acceleration voltage of 100 kV.

3. Results and discussion

3.1. Hydrothermal synthesis of Ag Nanoparticles. Fig. 1 shows absorption spectra of aqueous AgNO₃/PVP solutions in the reactor at 40 MPa and at 250 °C for different flow rates. They are characterized by a broad band around 400 nm attributed to the surface plasmon (SP) band of Ag nanoparticles, suggesting the formation of Ag nanoparticles with broad size distribution. In the absence of PVP, no absorption band was observed in the visible region, indicating that PVP acts as a reducing agent as well as a protective agent for the formation of Ag nanoparticles under hydrothermal conditions. The absorbance at 400 nm increases with decreasing flow rate, suggesting the increased yield of Ag nanoparticles formation due to the long reaction time for the low flow rate. As the inner volume of the reactor is about 1 cm³, the mean reaction times are 1, 2 and 5 min for flow rates of 1.0, 0.5 and 0.2 cm³/min, respectively. It is also found that the SP band is slightly blue-shifted with increasing flow rate, implying the formation of smaller particles for higher flow rate.

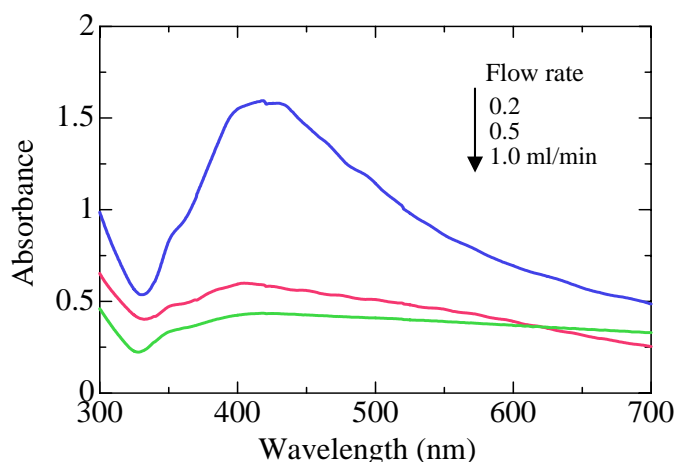


Fig. 1. Absorption spectra of AgNO₃/PVP aqueous solutions in the reactor at 250 °C and 40 MPa for different flow rates.

Products of hydrothermal synthesis were recovered from the outlet of the back-pressure regulator and subjected to TEM observations. Fig. 2 displays the TEM images showing Ag nanoparticles synthesized at 250 °C and 40 MPa for different flow rates. For flow rate of 0.2 cm³/min, small particles of less than 50 nm and somewhat large particles between 50 and

150 nm in diameter are observed. On the other hand, only small particles of less than 50 nm are observed for flow rate higher than 0.5 cm³/min. These observations are consistent with the spectral shift of the SP band in Fig.1. As aforementioned, the lower flow rate is, the longer reaction time is. The growth and agglomeration of nanoparticles proceed for the longer reaction time, leading to the formation of larger nanoparticles.

The size distribution has been estimated from TEM images. The results are given in Fig. 3. They show the similar size distribution for all flow rates: the higher population at the smaller particle size region. For flow rate of 0.2 cm³/min, it appears that large nanoparticles of 20 – 100 nm in diameter are preferentially produced, again suggesting the growth of particle size due to the long reaction time.

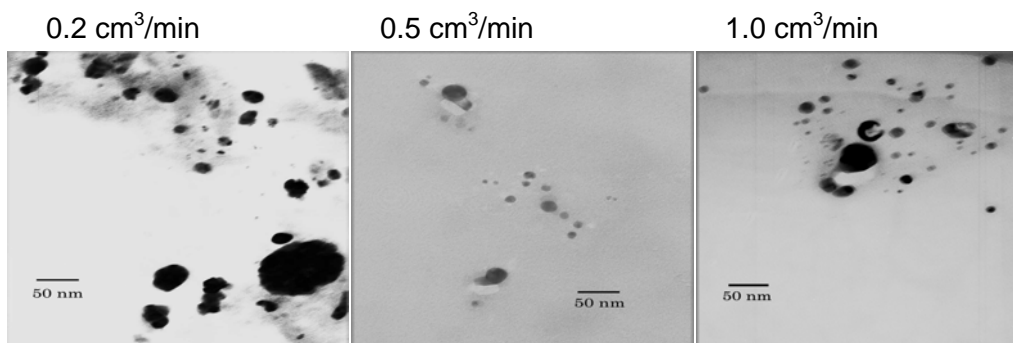


Fig. 2. The TEM images showing Ag nanoparticles synthesized at 250 °C and 40 MPa for different flow rates.

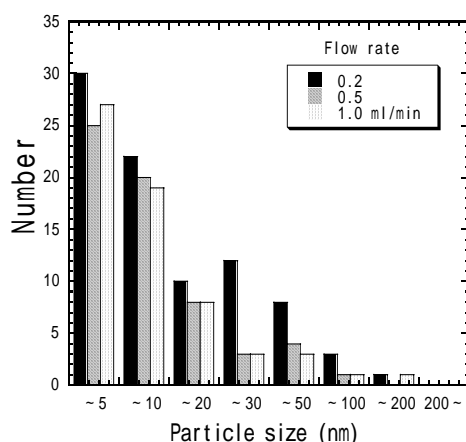


Fig. 3. Particle size distribution of Ag nanoparticles synthesized at 250 °C for different flow rates. P = 40 MPa.

Absorption spectra of AgNO₃/PVP aqueous solutions in the reactor at 300 and 350 °C are shown in Fig. 4 for different flow rates. They are characterized by the SP band of Ag nanoparticles developing around 400 nm. The influence of flow rate is almost the same as that for 250 °C. The increase in the absorbance at 400 nm and the blue-shift of the SP band are observed with decreasing flow rate. It is found that a broad shoulder appears around 500 – 600 nm for 350 °C and flow rate of 0.2 cm³/min, indicating the formation of fairly large nanoparticles possibly due to the progressive growth and agglomeration of nanoparticles under such conditions. More interestingly, the total intensity of the SP band for 350 °C is lower than that for 300 °C in spite of the rise of temperature. We also observed that the color of the dispersions collected for 350 °C was weaker than those for 300 °C, suggesting the low yield of Ag nanoparticles formation for 350 °C.

In accordance with absorption spectra, TEM images of Ag nanoparticles synthesized at 300 °C are analogous to those synthesized at 250 °C. Only small nanoparticles of less than 50 nm are observed for flow rates of 0.5 and 1.0 cm³/min, while relatively large particles of

~100 nm are formed for 0.2 cm³/min. The size distributions obtained by the analysis of TEM images are also quite similar to those observed for 250 °C.

Somewhat different results are obtained for Ag nanoparticles synthesized at 350 °C. The left panel in Fig. 5 shows TEM image of Ag nanoparticles synthesized at 350°C, 40 MPa and 0.2 cm³/min. While small particles of less than 30 nm as well as fairly large particles of more than 100 nm are observed there, no particles with intermediate size between 30 and 100 nm are found in any TEM images for 0.2 cm³/min. This behavior is clearly shown by the particle size distribution in Fig. 5b, demonstrating the bimodal shape of the distribution for all flow rates. The formation of fairly large particles is in agreement with the shoulder around 500 – 600 nm appeared in absorption spectra.

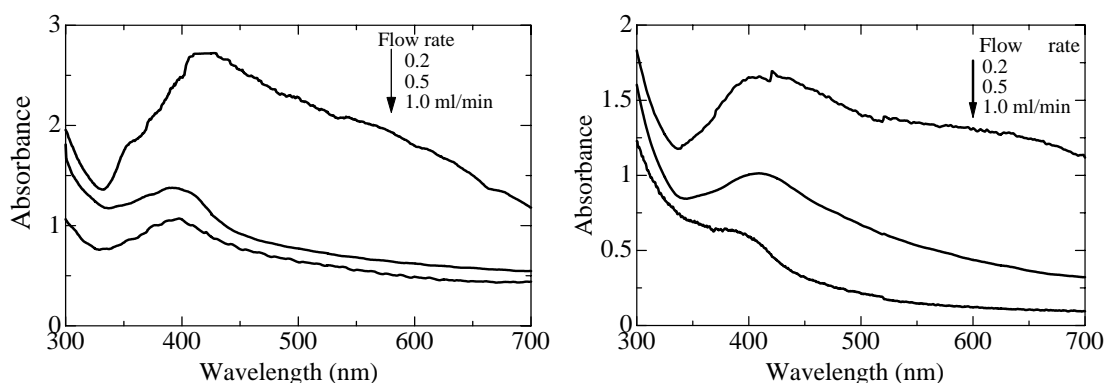


Fig. 4. Absorption spectra of AgNO₃/PVP aqueous solutions in the reactor at 300 °C (left panel) and 350 °C (right panel) for different flow rates. P = 40 MPa

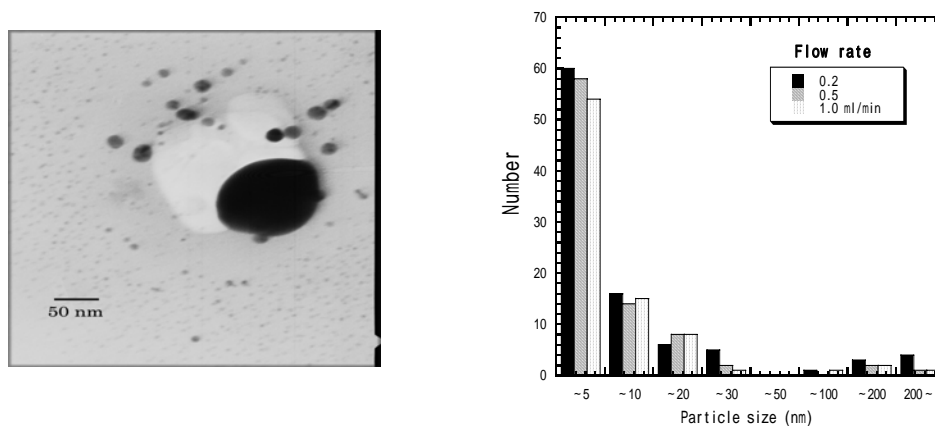


Fig. 5. TEM image of Ag nanoparticles synthesized at 350°C, 40 MPa and 0.2 cm³/min (left panel). Particle size distribution of Ag nanoparticles synthesized at 350°C and 40 MPa for different flow rates (right panel).

3.2. Effect of hydrothermal treatments. To understand how the particle size is determined during hydrothermal synthesis, it is helpful to investigate the change in the size and morphology of Ag nanoparticles as a result of hydrothermal treatments. To this end, we prepared Ag nanoparticles at ambient temperature and pressure by the photochemical method and then exposed them to the hydrothermal environment.

For the photochemical preparation of Ag nanoparticles, aqueous solutions of AgNO₃ (0.3 mM) and PVP (3 wt%) were irradiated by the UV light of 120 W low-pressure mercury lamp for 7-8 hours. The absorption spectrum of the dispersion thus prepared exhibits the sharp SP

band at 410 nm (dashed line in Fig. 6), indicating the formation of Ag nanoparticles. TEM observations revealed that spherical Ag nanoparticles with 5-20 nm in diameter were produced. The dispersions were injected into the reactor for the hydrothermal treatment under the same conditions as those of the hydrothermal synthesis and collected from the outlet of the back-pressure regulator. Absorption spectra of the dispersions in the reactor were monitored using a spectrophotometer. The changes in the size and morphology of nanoparticles were examined by TEM observations.

Fig. 6 shows the absorption spectra of the dispersions in the reactor at 250, 300 and 350 °C for different flow rates. The spectrum at room temperature is also presented by the dashed line for a reference. At 250 °C, almost no evolution of the spectral shape is observed except for the increase in absorbance in the short-wavelength region and the slight blue-shift of the SP band at 400 nm. As temperature is raised to 300 °C, further increase in absorbance and the small blue-shift of the SP band are observed. It is noted that some of Ag⁺ ions in the dispersions remained unreacted during the photochemical preparation. They might be reduced on the hydrothermal treatment of the dispersions, leading to the additional formation of Ag nanoparticles and therefore the growth of the SP band as seen in Fig. 6. It is important to note that the collected dispersions looked a little turbid due to the formation of certain particles composed of PVP, which is predominantly responsible to the increasing absorbance in the short-wavelength region due to the light scattering.

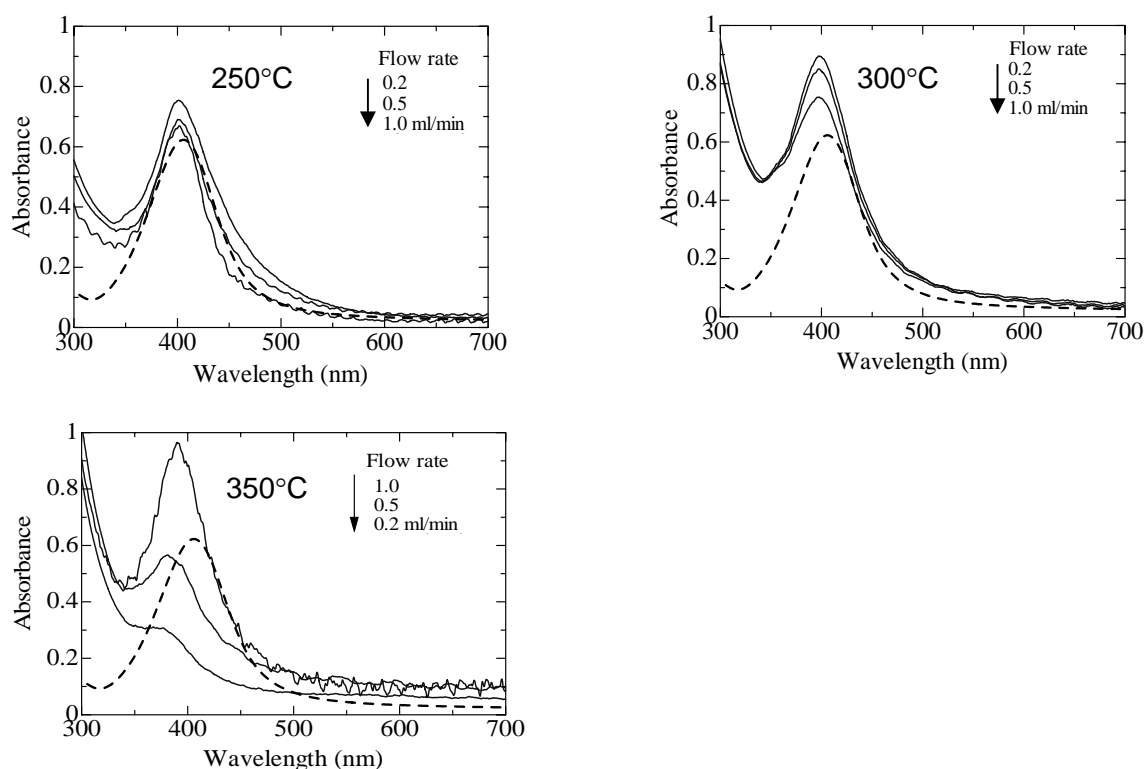


Fig. 6. Absorption spectra of the dispersions containing Ag nanoparticles and PVP in the reactor at 250, 300 and 350 °C for different flow rates. Dashed lines represent the absorption spectrum of the dispersion at room temperature.

More interestingly, absorption spectra observed at 350 °C show that lowering flow rate, i.e., increasing reaction time is accompanied by the decrease and blue-shift of the SP band, suggesting the disappearance of Ag nanoparticles in the dispersions. The decolorization was also found for the dispersion treated at flow rate of 0.2 cm³/min. We have interpreted this

observation in terms of the substantial depression of the protective action of PVP and therefore the dissolution of Ag nanoparticles in water at this temperature. It is interesting to point out that water at 350 °C and 40 MPa can be regarded as subcritical water, which possesses unusual properties such as large ion product, high diffusivity and high chemical reactivity.

TEM images of Ag nanoparticles after the hydrothermal treatment at 350 °C are shown in Fig. 7a. In accordance with expectations based on absorption spectra, a number of nanoparticles of less than 10 nm are found in TEM images, indicating that Ag nanoparticles become smaller during the hydrothermal processing. Simultaneously, fairly large nanoparticles of more than 200 nm are always observed, suggesting the agglomeration of nanoparticles due to the depression of the protective action of PVP. Fig. 7b presents the size distribution of Ag nanoparticles treated at 350 °C for different flow rates. The tendency of Ag nanoparticles to become smaller and agglomerate at the same time is again recognized for flow rate of 0.2 cm³/min.

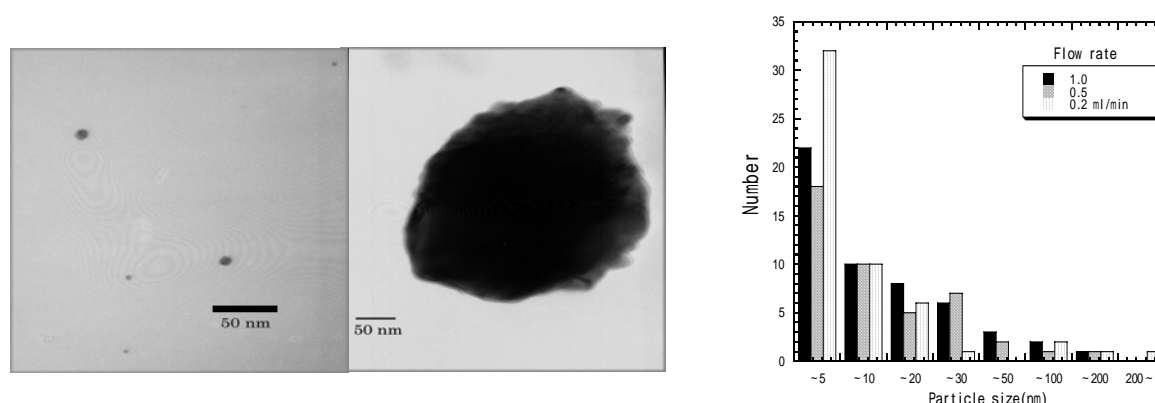


Fig. 7. TEM images (left panel) and the size distribution (right panel) of photochemically prepared Ag nanoparticles after hydrothermal treatments at 350 °C. The flow rate for TEM images is 0.2 cm³/min.

In view of above results, we can infer the formation mechanism of Ag nanoparticles during the hydrothermal synthesis. For 250 and 300 °C, PVP maintains the protective action and therefore the growth of Ag nanoparticles to more than 100 nm is suppressed even for the long reaction time of about 5 min. In contrast, the depression of the protective action of PVP at 350 °C promotes the aggregation of nanoparticles. At the same time, the dissolution of Ag nanoparticles in water suppresses the formation and growth of nanoparticles, leading to lower yield of Ag nanoparticles formation in consistence with lower intensity of the SP band in Fig. 4b. This effect also suppresses the growth of nanoparticles. Considering the fact that almost no particles with intermediate size between 30 – 100 nm are observed for the dispersions prepared at 350 °C, once Ag nanoparticles attain to 100 nm in diameter, they might grow up without the dissolution in water.

4. Conclusions

The hydrothermal synthesis of Ag nanoparticles using the flow-type reactor has been demonstrated. The size distribution of Ag nanoparticles is dependent on the processing temperature and flow rate. The hydrothermal treatment of Ag nanoparticles previously prepared by photochemical method suggests the substantial depression of the protective action of PVP and therefore the dissolution of Ag nanoparticles in water when treated at 350°C, which plays an important role in the formation mechanism of Ag nanoparticles in the hydrothermal synthesis. The technique developed in this study could be of practical

importance to realize the consecutive production of Ag nanoparticles with controlled size distribution.

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