

PREPARATION OF SIZE-CONTROLLED SILVER NANOPARTICLES BY THE HYDROTHERMAL METHOD

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Noble metal nanoparticles (NPs) have been extensively studied owing to many intriguing properties such as high catalytic activity, remarkable optical properties arising from the localized surface plasmon resonance, and so on. In recent years, Ag NPs have been drawing much attention as a new material for constructing the wiring patterns on electric circuit boards by means of the printing technology. From the viewpoint of such applications, developing the cost-effective method to produce a large quantity of size-controlled Ag NPs is an important subject for study. We recently examined the hydrothermal synthesis of Ag NPs by using the flow-type high-temperature high-pressure reactor and demonstrated that it would be promising for the large-scale synthesis of Ag NPs [1]. Here, we report that the size and morphology of Ag NPs produced by this method can be controlled by adjusting the reaction conditions such as temperature, pressure and flow rate.

Fig. 1 shows the schematic diagram of the flow-type high-temperature high-pressure reactor system used in this study. This reactor system was designed to allow the rapid mixing of two kinds of solutions under hydrothermal conditions. Two kinds of aqueous solutions containing 1.5 mM AgNO₃ and 30 g dm⁻³ polyvinylpyrrolidone (PVP) (solution A) or 15 mM sodium citrate and 30 g dm⁻³ PVP (solution B) were prepared with a distilled water. These solutions were individually fed into the tubular reactor made of stainless steel (1/8 inch o.d and 1.755 mm i.d) by two intelligent high pressure pumps (Jasco co. Pu-2080) and mixed at a T-shaped junction (SS-200-3, Swagelok) inside of the reactor. An orifice having a pinhole with 0.5 or 1.0 mm diameter was installed inside the T-shaped junction if needed. The reactor was immersed in a thermostated salt bath to control reaction temperature between 200–350°C and pressure was adjusted between 15–40 MPa by a back-up pressure regulator. The produced Ag NPs were analyzed by an optical absorption spectroscopy with a V-530 UV-vis spectrophotometer (Jasco co.) and a transmission electron microscopy (TEM) with an H-7000 microscope (Hitachi).

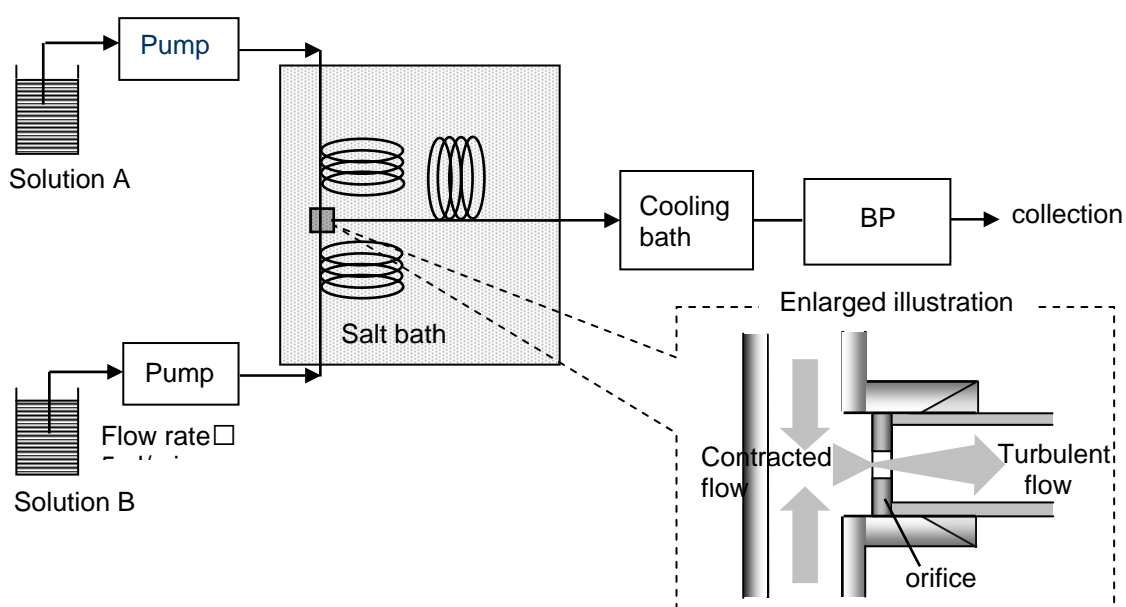


Figure 1: Schematic diagram of experimental reactor system used in this study.

We began with synthesizing Ag NPs at different pressures (15, 20, 23, 30, 40 MPa) and at fixed temperature, 300°C. The absorption spectra of obtained colloidal solutions were characterized by a distinct band at about 400 nm for all pressures, which was attributed to the localized surface plasmon (LSP) resonance of Ag NPs. The intensity of LSP band increased with pressure from 15 MPa to 20 MPa while it turned to decrease above 23 MPa. It was found that yellow precipitate was accumulated inside the filter at pressures above 30 MPa, indicating the considerable aggregation of Ag NPs. The TEM image and size distribution of Ag NPs obtained under typical condition (23 MPa) were shown in Fig. 2. The average diameters of Ag NPs estimated from TEM images are 13.8 ± 5.3 , 17.5 ± 6.8 , and 18.1 ± 6.6 nm for 15, 20, and 23 MPa, respectively. At 30 and 40 MPa, most of NPs are larger than 100 nm and the size was rather inhomogeneous.

Next, Ag NPs were synthesized at fixed pressure, 20 MPa, and at different temperatures, 200, 250 and 350°C. For all temperatures, the sizes of obtained Ag NPs were less homogeneous than those for 300°C. In particular, the colloidal solution obtained at 200°C showed no distinct SP band, suggesting that only small amount of Ag NPs were produced. It is interesting that Ag NPs obtained at 350°C have a variety of shapes like rods, triangles and squares, implying a possible control of morphology by tuning the reaction condition. However, most of Ag NPs obtained at this temperature were larger than 100 nm. Based on the above observations, it is concluded that the optimal reaction conditions for the synthesis of fine and homogeneous Ag NPs are $T=300^\circ\text{C}$ and $P=20\sim 23$ MPa, respectively.

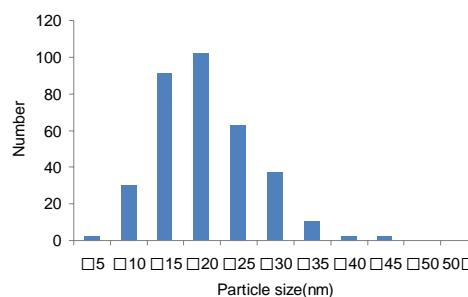
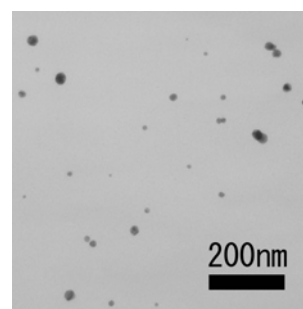
We finally examined the effect of an orifice installed inside the reactor. As seen in Fig. 1, the flow path is narrowed by the orifice. This causes the contracted and turbulent flow before and after the orifice, resulting in the effective mixing of two reaction solutions at the T-shaped junction. When the orifice with 0.5 or 1.0 mm diameter was installed, the average sizes of Ag NPs produced at 300°C and 20 MPa were 13.7 and 16.4 nm, respectively. These values are significantly smaller than that without the orifice inside the reactor (17.5 nm). Furthermore, the size distribution became more homogeneous when we used the orifice. It is thus obvious that the use of orifice is of benefit for the synthesis of fine and homogeneous Ag NPs by the present method.

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References:

[1] N. Kometani, et al., *J. Soc. Mater. Sci. Jpn. (Zairyo)*, **58** (2009) 481-485.



Figures: TEM image and size distribution of Ag NPs prepared at 300°C and 23 MPa.