

Preparation of Silver Nanoparticles via Continuous Hydrothermal Synthesis Method

(連続式水熱合成法による銀ナノ粒子の調製)

Expected graduation: 2023.9

Environment Systems 47216782 LI Yanchen

Supervisor: Associate Professor Akizuki Makoto

Key words: *Ag nanoparticles, Subcritical water, Continuous system, Size control*

1. Background

Silver nanoparticles, one of metal nanomaterials, have distinct physical, chemical and biological properties. It is widely used in medical products to sterilize, biosensors, catalyst and so on. The smaller the size of Ag nanoparticles is, the larger the specific surface area is, thus improving its antibacterial property. The conventional methods for preparing Ag nanoparticles have obvious disadvantages: Chemical methods have drawbacks including usage of complex chemical ingredients and toxic reducing agents. Preparation by vacuum-based physical techniques is more environment friendly but the complicated vacuum operation and low production rate limit its wide application.

On the other hand, continuous hydrothermal synthesis (CHS) is one of the methods to synthesize metal oxides. In this method, by mixing ScH_2O with a metal salt solution, metal ions are hydrolyzed in supercritical water to form hydroxides, which are then dehydrated to metal oxides. At the supercritical region, fast reaction rate and low solubility can lead to an extremely high nucleation rate, which allows the formation of nano-sized particles. CHS has advantages of high productivity (continuous production and collection of target products) and easy control of particle size (rapid heating and rapid cooling of the reaction fluid could lead to finer nanoparticles and stronger controllability of the particle size).

In a previous study, it has been confirmed that metal silver was obtained under supercritical conditions (380°C to 430°C) without reducing agent^[1], which may be because Ag is thermodynamically more stable than Ag_2O at this temperature range (in general, the obvious decomposition of Ag_2O is above 300°C or even 350°C). And it is hypothesized that, similar to the formation of metal oxide nanoparticles, Ag_2O is formed from a silver salt solution in supercritical water before it is converted to Ag nanoparticles.

Thus, it is feasible to produce Ag nanoparticles, instead of the commonly obtained metal oxide nanoparticles, in one step by this method. It is worth exploring whether the preparation and particle size control of AgNPs can be achieved under subcritical conditions at lower temperatures, which would be a good complement to nano-silver preparation methods.

2. Research Objective

Considering that the temperature range for the conversion of Ag_2O to Ag can be below the supercritical point (374°C, 22.1 MPa), it's possible that nano-silver can be formulated even under subcritical conditions (temperature below supercritical conditions) without requiring the use of reducing agents. Therefore, this study aims to achieve the one-step preparation of regular Ag nanoparticles by CHS under subcritical conditions and explore the preparation conditions (including concentration, reaction time, temperature and so on) to realize size-controllable synthesis.

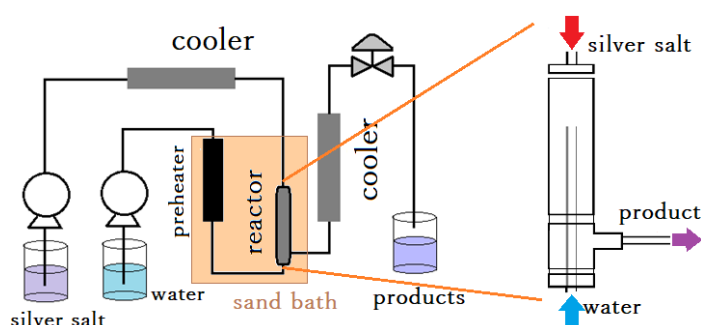


Fig. 1. The apparatus for nanoparticles synthesis

3. Experimental Method

Experiments were conducted using the flow-type reaction apparatus with a redesigned reactor with reference to the Nozzle reactor^[2] shown in Fig.1. The reactor consists of inner diameter 3.75 mm and length 160 mm, and the water tube type is 1/16 inch. Since the synthesis of metal nanoparticles in continuous system is prone to clogging in pipeline, this reactor is designed to prevent clogging and make the reaction proceed smoothly. Silver salt solution was used as a raw material, mixed with hot distilled water heated in a sand bath, started reaction in the reactor and ended in the cooler. The experimental conditions are shown in the Table 1. The system pressure for all the experiments was 25 MPa. TEM and XRD were used to observe the composition and morphology of products. ICP emission spectrometry was used to measure the concentration of silver ions in solution.

Table. 1 The Reaction Conditions

	T(°C)	Concentration of CH ₃ COOAg (mol/L)	Flow rates for scH ₂ O: silver salt (mL/min)	Molar ratio for PVP40: silver salt
a1~5	350	0.005	15:7.5	0, 1:2~1:20
b1~5	350	0.0025~0.03	15:7.5	1:20
c	350	0.005	15:5	1:20
c	350	0.005	14.3:5.7	1:20
c	350	0.005	13.3:6.7	1:20
c	350	0.005	12:8	1:20
c	350	0.005	10:10	1:20
d1~8	220~350	0.005	15:7.5*	1:20
e1~4	350	0.005	10:5~30:15 (time varies)	1:20

#Concentration and flow rates are all in ambient state.

* The flow rates were adjusted slightly to keep the residence time at about 3 s.

4. Results and Discussion

4.1 Synthesis of Ag nanoparticles at 350°C

From the experiment conducted firstly at 350°C without reducing agents, the XRD pattern of the products confirmed that metal silver was obtained instead of oxide; but it revealed problems: wide particle size distribution, the particle agglomeration, and the silver powder sticking to the reactor wall. Thus, a stabilizer polyvinylpyrrolidone with Mw40000(PVP40) was introduced into subsequent experiments. And it was effective in avoiding silver sticking to the wall so that sufficient amount of product, which was also confirmed as Ag by XRD, was obtained. Fig.2 shows that the products apparently had a narrower particle size distribution and smaller average particle size than that without stabilizer, although the difference of effect in the range of 5~100 g/L was not significant. This indicates that this stabilizer has the effect of preventing aggregation and preventing Ag nanoparticles overgrowth to some extent via CHS, which is consistent with previous studies^[1].

Fig.3 shows that the effect of residence time in the frame of 1.5~4.5 s is not significant, after the time exceeded 4.5 s, there was a slight increase in the average particle size. The time dependence was not reflected, perhaps because the reactions have been carried out thoroughly in this time frame.

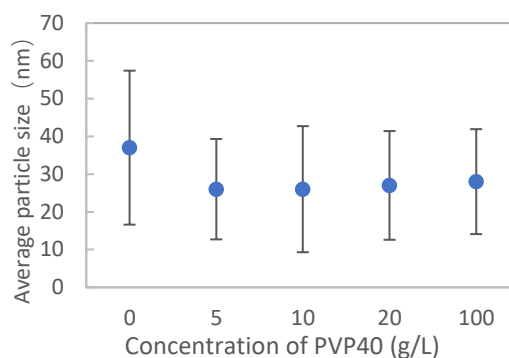


Fig.2. Effect of concentration of PVP40 on Ag nanoparticle size

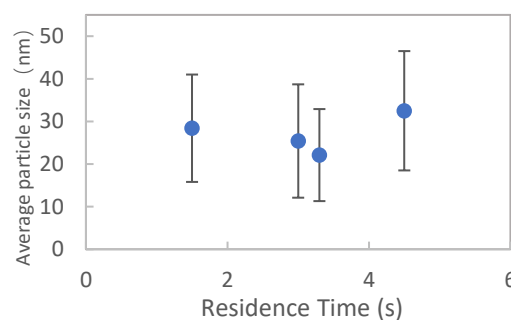


Fig.3. Effect of residence time on Ag nanoparticle size

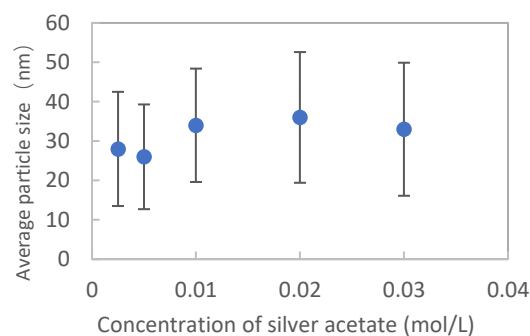


Fig.4. Effect of precursor concentration on Ag nanoparticle size

Fig.4 shows that when the concentration of silver salt is higher than 0.01 mol/L, the particle size increased compared with 0.005 mol/L. And from the corresponding TEM images, it can be observed that the higher the precursor concentration, the greater the tendency for larger nanoparticles to appear. This may be because that at high concentration, the particles could obtain fully growth.

According to Fig.5, as the proportion of water decreased and the proportion of salt increased, the average particle size showed a trend of decreasing and then increasing. The decreasing trend may be because the increased flow rate of salt results in the higher degree of supersaturation, which leads to smaller particle size^[3]; On the other hand, the reason of the increasing trend may be that the water was heated, its reduced proportion corresponds to a lower heating rate of the salt solution, which slows down the reaction rate and makes the particle size increase.

4.2 Synthesis of Ag nanoparticles at lower temperature

As shown in Fig.6, it was confirmed that metal Ag was obtained at 235, 245, 275, 300, 325, 350°C by XRD pattern of the products. Fig.7 shows that the conversion of Ag⁺ decreased with decreasing temperature below 300°C. Fig.8 shows that the average nanoparticle size and crystallite size both have a tendency to decrease with decreasing temperature. This is contrary to the result that higher temperatures led to smaller Ag nanoparticles in supercritical condition^[1]. This may be due to the fact that

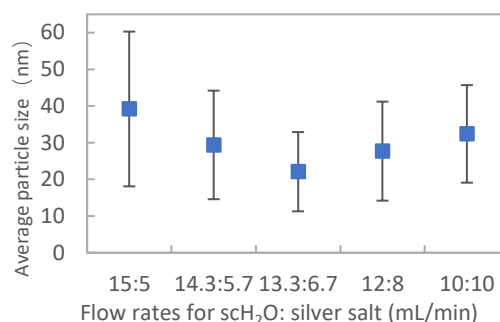


Fig.5. Effect of flow rates ratio on Ag nanoparticle size

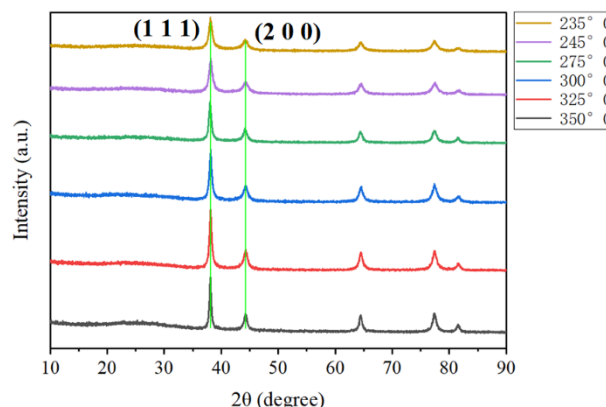


Fig.6. The XRD Pattern of products

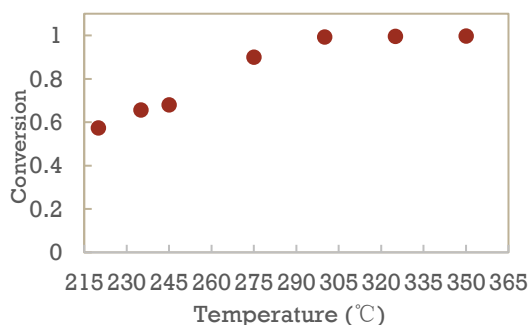


Fig.7. Effect of temperature on silver ion conversion

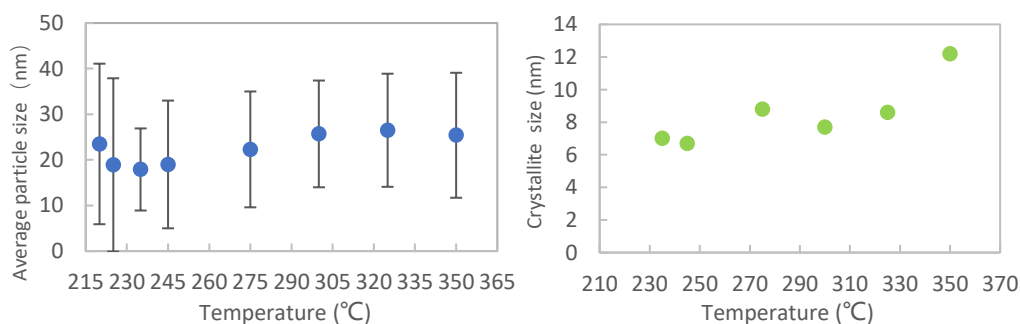


Fig.8. Effect of temperature on Ag nanoparticle size and crystallite size

in the range of 230 to 350°C, which is not close to the critical point of water, the precursor solubility increases with increasing temperature and therefore the degree of supersaturation decreases, the amount of nucleation decreases, and the particles grow to a greater extent. In the experiments at 220 and 225°C, the particle size distribution of the product particles was concentrated in two ranges, resulting in very large standard deviations, which indicated the presence of both smaller and larger particles. This

phenomenon can be seen more visually on Fig.9, and very small number of giant particles (300~400 nm) appeared, whose crystal plane spacing was obtained from the High-resolution TEM image, and a comparison with standard cards revealed that it is still metallic silver like other small particles.

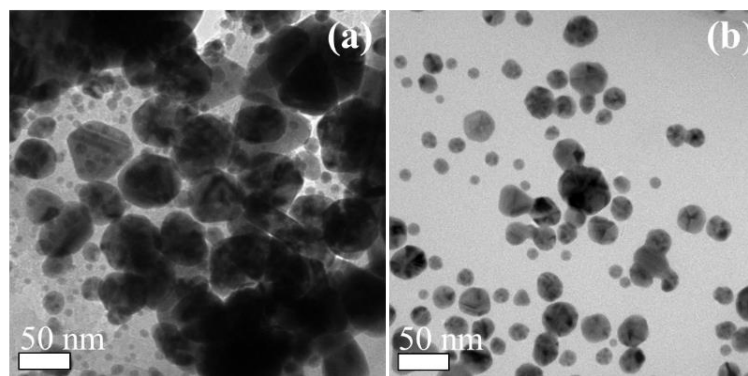


Fig.9. TEM images of product at 225°C (a) and 235°C (b)

4.3 Reactivity of Ag₂O in

subcritical water in batch reactor system

No previous studies have been recorded on the direct conversion of Ag₂O to Ag in supercritical or subcritical water. In aforementioned experiments, there was still no silver oxide when the temperature was lowered to 220°C. Therefore, two experiments were conducted to investigate the presence of silver oxide as an intermediate product in the preparation of Ag nanoparticles, using silver oxide powder as raw material in a batch reactor.

	T	Precursor	Residence Time
f	250°C	Ag ₂ O powder	30min
f	300°C	Ag ₂ O powder	30min

The XRD pattern of the products indicates that Ag₂O did not decompose

to Ag in these experiments (Fig.10). Thus it is possible that there is no step of thermal decomposition of Ag₂O in the continuous hydrothermal synthesis of nano-Ag, or nano-Ag can only be synthesized under subcritical conditions using salt solutions as raw materials rather than Ag₂O.

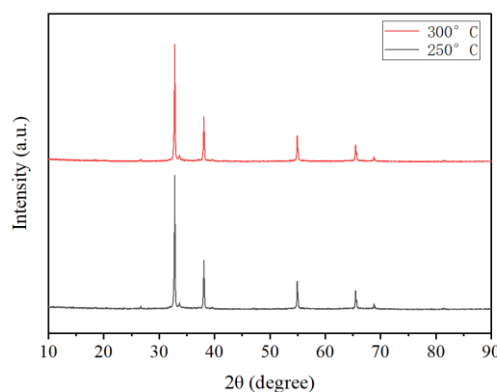


Fig.10. The XRD Pattern of Ag₂O treated at 250 or 300°C

5. Conclusion and Prospect

In this study, AgNPs were successfully synthesized in one step by continuous hydrothermal synthesis under subcritical conditions without the use of reducing agent. The particle size control of the products was also investigated. The addition of stabilizer PVP40 and the reduction of precursor concentration were effective in reducing the particle size and narrowing the particle size distribution. It is possible that for the preparation of AgNPs, 350°C is not low enough for exhibiting the effect of residence time on particle size and conversion, so time dependence below 300°C (where the conversion begins to decrease) or a wider time frame requires further investigation. The variation of particle size with flow rate ratios implies that the size of AgNPs can be adjusted directionally. At lower subcritical temperatures, it is possible to synthesize particles with sizes similar to those under supercritical conditions (15-30 nm), which is conducive to saving energy and easing the requirements for preparation equipment; And considering the abnormal grain growth and low conversion rate at temperatures lower than 225°C, the applicability of the corresponding products is low, but the tendency of particle size to decrease with temperature(235~350°C) can provide more options depending on the application requirements.

References

- [1] G. Aksomaityte, M. Poliakoff, E. Lester, *Chemical Engineering Science*. **85**, 2-10(2013) [2] E. Lester et al. *The Journal of Supercritical Fluids*. **37**, 209-214(2006) [3] S. Kubota, T. Morioka, et al. *The Journal of Supercritical Fluids*. **86**, 33-40(2014).