

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Silver Nanoparticles by chemical reduction method.

Silver nanoparticles have specific optical properties indicated by the plasmon extinction band in the UV-visible and NIR regions. This caused by the collective oscillation of the electrons around the particles. Silver nanoparticles can be characterized by a color change in the solution and by UV-Visible extinction spectra.

The reduction of silver salt by different reducing agents generally yields different size, size distribution, and morphology silver nanoparticles. In this work, silver nanoparticles were synthesized by chemical reduction method with various reducing agents in order to find an appropriate reducing agent for thermal reduction of sprayed silver salt. This method requires the reducing agent having no reduction ability at room temperature (before nebulization) then reduce the silver ions at high temperature (after nebulization) in order to let the reaction occur only in the aerosol droplet. Therefore, reducing agents used in this section were weak reducing agents such as ethylene glycol, glycerol, glucose, and sodium citrate. Furthermore, these reducing agents are environmental friendly.

Concentration of silver nitrate, concentration reducing agent used in this section and temperature that observed the change in color of the solution (indicated the formation of silver nanoparticles) was shown in Table 4.1. The UV-Visible extinction spectra of synthesized silver nanoparticles by various reducing agent was shown in Figure 4.1 and their corresponding photographs shown in Figure 4.2

Table 4.1 Condition in the synthesis of silver nanoparticles by chemical reduction method.

Reducing agent	[AgNO ₃] (10 ⁻³ mol/L)	Concentration of reducing agent	Reaction temperature (°C)
ethylene glycol	1.0	50 % v/v	80
glycerol	1.0	50 % v/v	100
glucose	1.0	0.1 mol/L	100
Sodium citrate	1.0	0.1 mol/L	-*

*not observe the color change of the solution

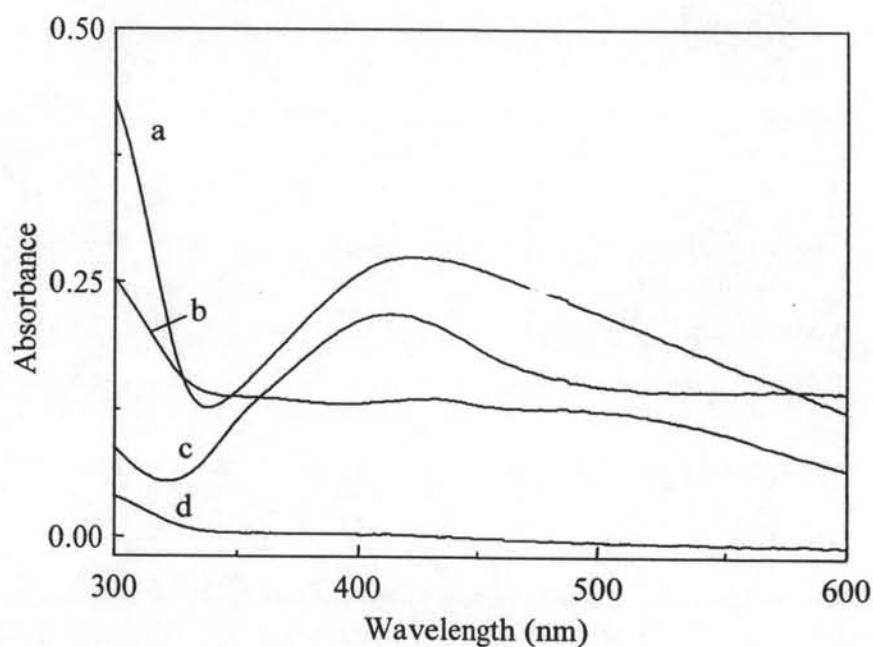


Figure 4.1 UV-Visible extinction spectra of synthesized silver nanoparticles at various reducing agents: (a) ethylene glycol, (b) glycerol, (c) glucose, and (d) citrate.

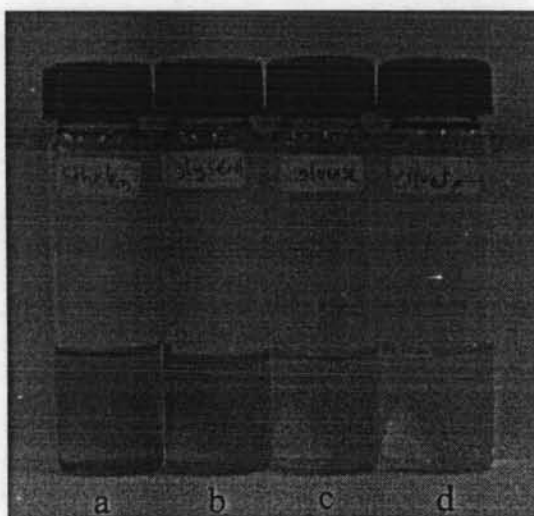


Figure 4.2 Photograph of synthesized silver nanoparticles reduced by various reducing agents: (a) ethylene glycol, (b) glycerol, (c) glucose, and (d) citrate.

Silver nanoparticles synthesized by ethylene glycol, glycerol, and glucose had yellow color at the beginning and the color gradually changed to red and then black. UV-Visible extinction spectra show absorption maxima about 420 nm and broadening. The result from UV-Visible extinction spectra and the color change indicated that the size of synthesized silver nanoparticles was large with a broad size distribution. This comes from the fact that weaker reducing agent has longer period of nucleation step and stabilizers were not added to protect the particle-to-particle interaction. Thus, large particles with broad size distribution were yielded.

In citrate reduction, when the mixture of silver nitrate and sodium citrate was heated to 100 °C and maintained at this temperature for 30 min. No color changing was observed. UV-Visible spectra of this solution did not show any peak around 400 nm as shown in Figure 4.1(d). These results indicated that the reduction did not occur and silver nanoparticles were not formed in solution. This suggested that the reduction potential of citrate was too low to reduce silver ion to silver particles.

From the result, the appropriate reducing agents for thermal reduction of sprayed silver salt are ethylene glycol, glycerol, and glucose. However, when ethylene glycol and glycerol were used, the nebulizer cannot generate droplets and causes the emulsion in nebulizer reservoir because the viscosity of ethylene glycol and glycerol is too high compared to water. This nebulizer was designed for water based solution. Thus, the appropriate reducing agent was glucose.

4.2 Synthesis of silver nanoparticles by thermal reduction of sprayed silver salt.

Thermal reduction of sprayed silver salt method was shown in Figure 4.3. In this method, the mixture of silver nitrate and glucose is nebulized into the tubular reactor. It is believed that the reaction occurs in one drop that acts as a *micro-reactor*. Silver nanoparticles are obtained separately in one drop and produced one particle per drop. Therefore, particle size and size distribution of silver nanoparticles can be controlled without any stabilizer or capping agent. Then, the synthesized silver nanoparticles were trapped in cold water. Silver nanoparticles formations were observed by the color changing of the trapped solution which getting started changing from colorless to bright yellow.

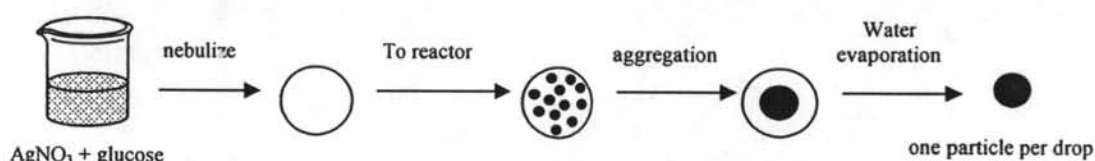
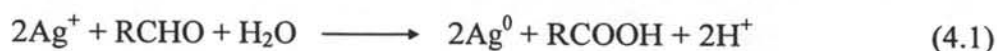
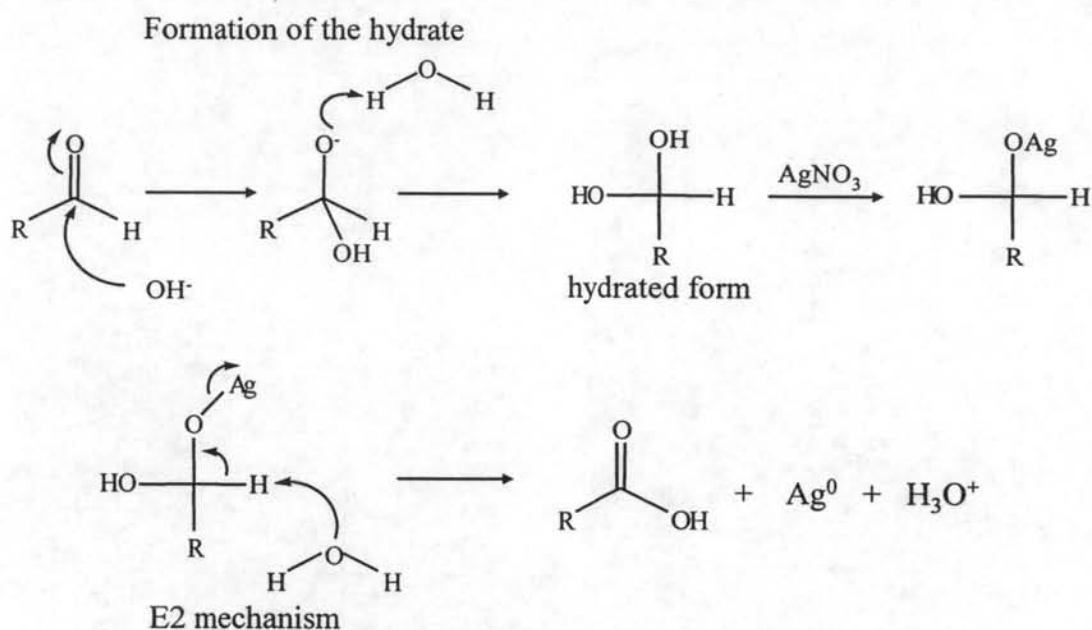


Figure 4.3 Thermal reduction of sprayed silver salt

In a micro reactor the reaction occurs as follows:



The proposed reaction mechanism is as follows:



UV-Visible extinction spectra of synthesized silver nanoparticles by thermal reduction of sprayed silver salt method are shown in Figure 4.4.

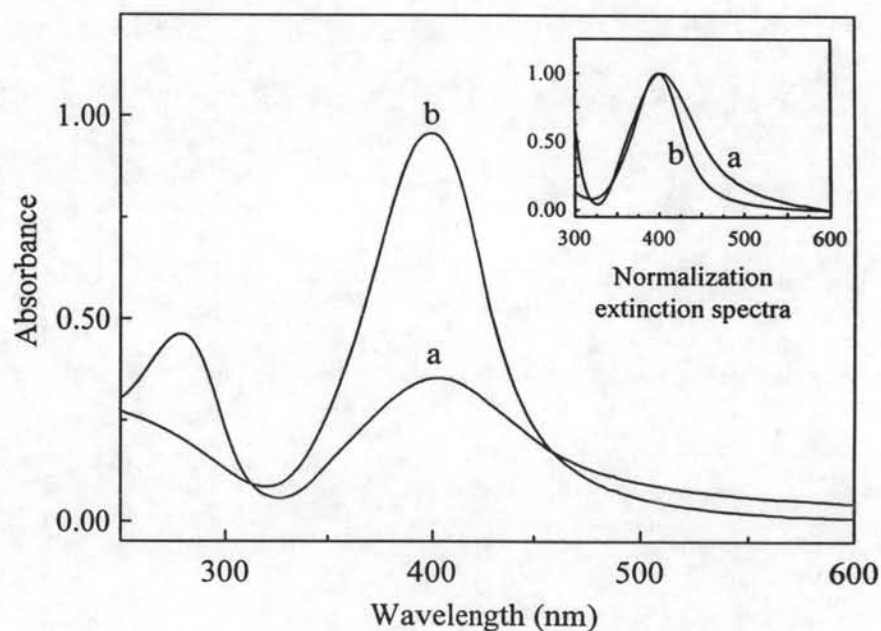


Figure 4.4 UV-Visible extinction spectra of synthesized silver nanoparticles: (a) without ammonia solution, (b) with ammonia solution. Normalized spectra are shown in the inset.

Originally no catalyst was used in the process. But the reaction did not complete in each individual droplet. The increasing of intense of yellow color in trapping product was also observed after left over for a period of time. These indicated that there were active silver ions remained in trapping solution. The active silver ion caused aggregation observed by UV-Visible extinction spectrum in Figure 4.4(a). The reaction rate was too slow to complete within the tubular reactor. Therefore, the ammonia solution was used as a catalyst in order to increase the rate of the reaction. The ammonia solution catalyzed the reaction because formaldehyde and glucose are oxidized easier under basic conditions as shown in Equation 4.1. As a result, UV-Visible spectrum of synthesized silver nanoparticles when ammonia solution was used as a catalyst has higher intensity with lower FWHM.

In order to observe the aggregation of synthesized silver nanoparticles. UV-Visible spectra of trap water were collected as a function of time as shown in Figure 4.5.

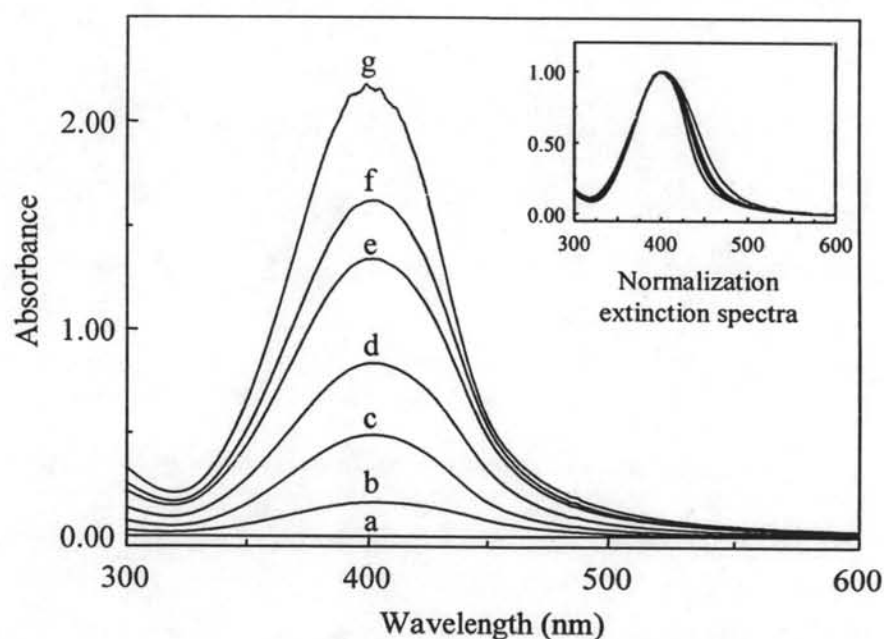


Figure 4.5 UV-Visible spectra of synthesized silver nanoparticles measured at the reaction time: (a) 0 min, (b) 10 min., (c) 20 min., (d) 30 min., (e) 40 min., (f) 50 min., (g) 60 min. Normalized spectra are shown in the inset.

From Figure 4.4, there were no significant change in the position of the extinction maxima and FWHM. This indicates that there are no active silver ions remain in trap product. These synthesized silver nanoparticles are stable because the carboxylic by-product (as shown in Equation 4.1) can stabilize the surface of silver as citrate ion [33] as Figure 4.6.

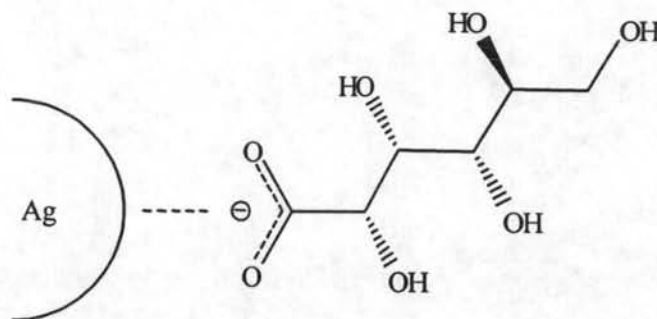


Figure 4.6 Proposed interaction of carboxyl and the surface of silver nanoparticles.

4.3 Preliminary study on the possibility of characterization technique (UV-Visible spectroscopy).

At the beginning of this research, silver nanoparticles were synthesized by thermal reduction of sprayed silver salt method and observed the color change in the solution which changed from colorless to light yellow. When measuring the UV-Visible spectrum of this trapping solution, the spectrum did not show any peak around 400 nm as shown in Figure 4.7. This indicated that the yellow solution was not the solution of silver nanoparticles but it was the solution of thermal deformation of glucose. This occurred because the temperature in tubular reactor was too high.

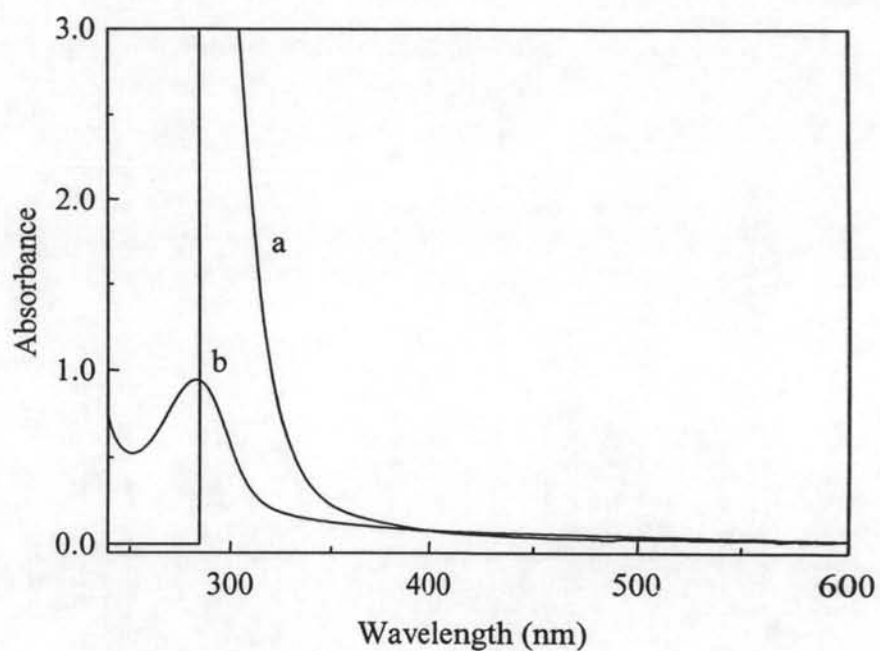


Figure 4.7 UV-Visible extinction spectra of (a) trapping solution and (b) its diluted counterpart.

Therefore, it is important to measure all the precursor UV-Visible spectra before and after nebulization in order to study the interference of all precursor spectra. In this study, all precursors spectra were collected and compared with the spectrum of synthesized silver nanoparticles as shown in Figure 4.8.

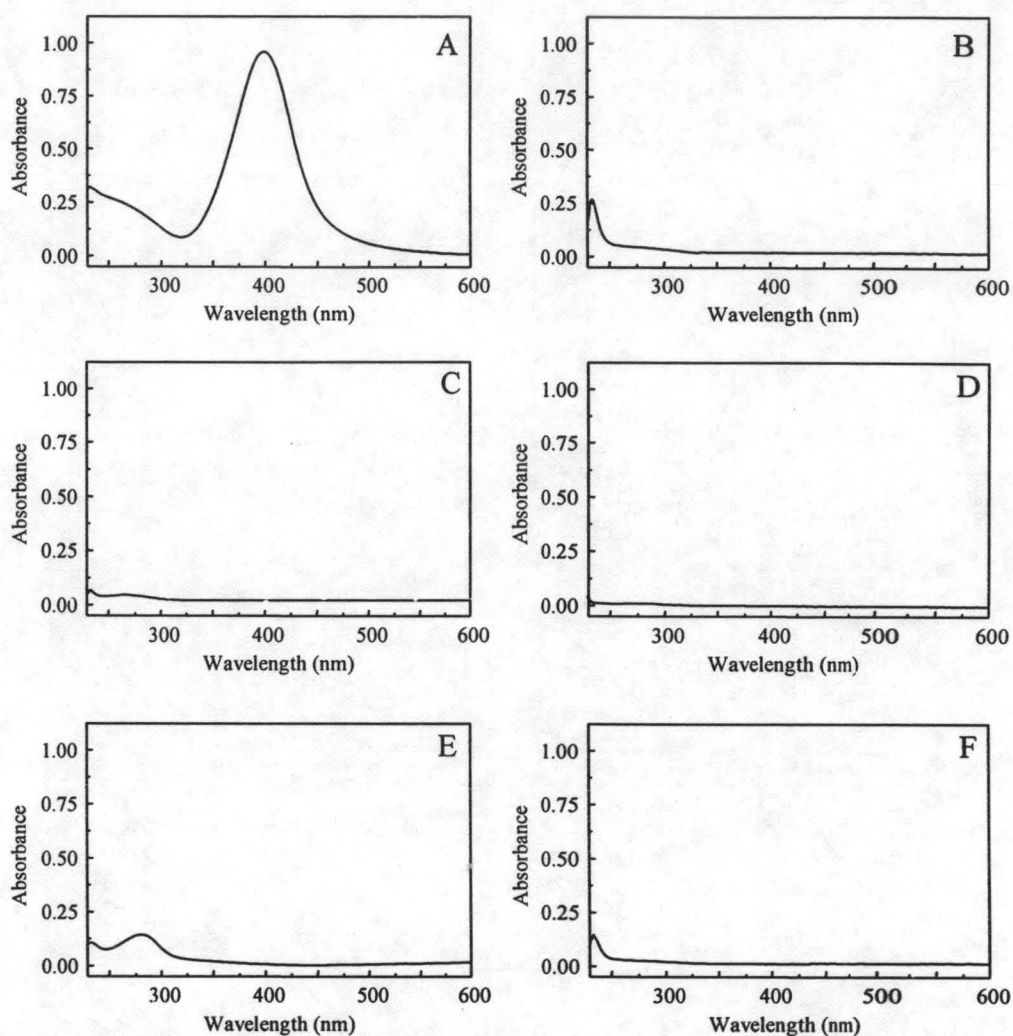


Figure 4.8 UV-Visible spectra of (A) synthesized silver nanoparticles, (B) silver nitrate and glucose, (C) nebulized glucose, (D) glucose, (E) nebulized silver nitrate, and (F) silver nitrate.

All the precursors spectra did not interfere with the spectrum of silver nanoparticles except the spectrum of nebulized silver nitrate which had a peak around 280 nm. The peak is assigned to the absorption of Ag_2^+ and the Ag_4^{2+} complexes [16]. The spectrum from Figure 4.8(B) indicated that the reaction did not occur when mixing the precursor in the nebulizer reservoir at room temperature.

4.4 Investigation of the various factors affecting the synthesis of silver nanoparticles by thermal reduction of sprayed silver salt method.

In this method, many factors such as concentration of precursor, droplet size, and type of carrier gas affecting on size, size distribution, and morphology of synthesized silver nanoparticles were investigated.

4.4.1 The concentration silver nitrate

In the spray pyrolysis method, the size of synthesized silver nanoparticles can be predicted by the droplet size that generates from nebulizer and the silver ion solution concentration. Here, we assumed that the reaction occurs in one drop, which converts all silver ions to silver nanoparticles and produced one silver nanoparticle per drop. The silver mass balance for each spherical particle is:



$$\frac{g_{\text{Ag}^0}}{M_{\text{Ag}^0}} = \frac{[\text{AgNO}_3] \cdot V_{\text{AgNO}_3}}{1000} \quad (4.2)$$

Volume of each drop is:

$$V_{\text{AgNO}_3} = \frac{4}{3} \pi r_{\text{drop}}^3 \quad (4.3)$$

Assuming that synthesized silver nanoparticles have spherical shape and the particle reach theoretical density ($\rho = 10.490 \text{ g/cm}^3$), we can find the volume and radius of silver particles as follows:

$$g_{\text{Ag}^0} = \rho_{\text{Ag}} V_{\text{Ag}^0} \quad (4.4)$$

$$g_{\text{Ag}^0} = \rho_{\text{Ag}} \frac{4}{3} \pi r_{\text{Ag}^0}^3 \quad (4.5)$$

Substituting Equation 4.2 and 4.3 in Equation 4.1, we get

$$\frac{\rho_{Ag} \frac{4}{3} \pi r_{Ag^0}^3}{M_{Ag^0}} = \frac{[AgNO_3] \cdot \frac{4}{3} \pi r_{drop}^3}{1000} \quad (4.6)$$

After some manipulation, we obtain

$$\left(\frac{r_{Ag^0}}{r_{drop}} \right)^3 = \frac{[AgNO_3] \cdot M_{Ag^0}}{1000 \cdot \rho_{Ag^0}} \quad (4.7)$$

Substitute $\rho_{Ag} = 10.490 \text{ g/cm}^3$ and $M_{Ag} = 107.87$ in Equation (4.7), we obtain

$$\frac{r_{Ag^0}}{r_{drop}} = 0.2174 [AgNO_3]^{\frac{1}{3}} \quad (4.8)$$

Substitute droplet size $r_{drop} = 1.5 \text{ } \mu\text{m}$ in Equation (4.8), we get

$$r_{Ag^0} = 0.3262 [AgNO_3]^{\frac{1}{3}} \quad (4.9)$$

where,

- g_{Ag} = mass of silver particle
- M_{Ag} = molecular weight of silver
- $[AgNO_3]$ = concentration of silver nitrate
- V_{AgNO_3} = volume of silver nitrate
- V_{Ag} = volume of silver particle
- ρ_{Ag} = density of silver metal
- r_{drop} = radius of droplet form nebulizer (μm)
- r_{Ag} = radius of silver particle (μm)

Thus, the final diameter of silver nanoparticle is proportional to the silver nitrate concentration as expressed in Equation 4.9. In our method, we assume that the reaction occurs under the same mechanism as that in the spray pyrolysis method. The Equation 4.9 was used to predict the size of synthesized silver nanoparticles and some result are shown in Table 4.2

Table 4.2 Theoretical prediction of size of synthesized silver nanoparticles at various in silver nitrate concentration.

Concentration of AgNO ₃ (mmol/L)	Predicted diameter of particle (nm)
1.0	65.24
0.7	57.92
0.5	51.78
0.3	43.67

The concentrations of silver nitrate were varied from 0.3, 0.5, 0.7 and 1.0 mmol/L in order to observe the change in UV-Visible extinction spectra of synthesized silver nanoparticles. UV-Visible extinction spectra of synthesized silver nanoparticles when various concentrations of silver nitrate were used are shown in Figure 4.9.

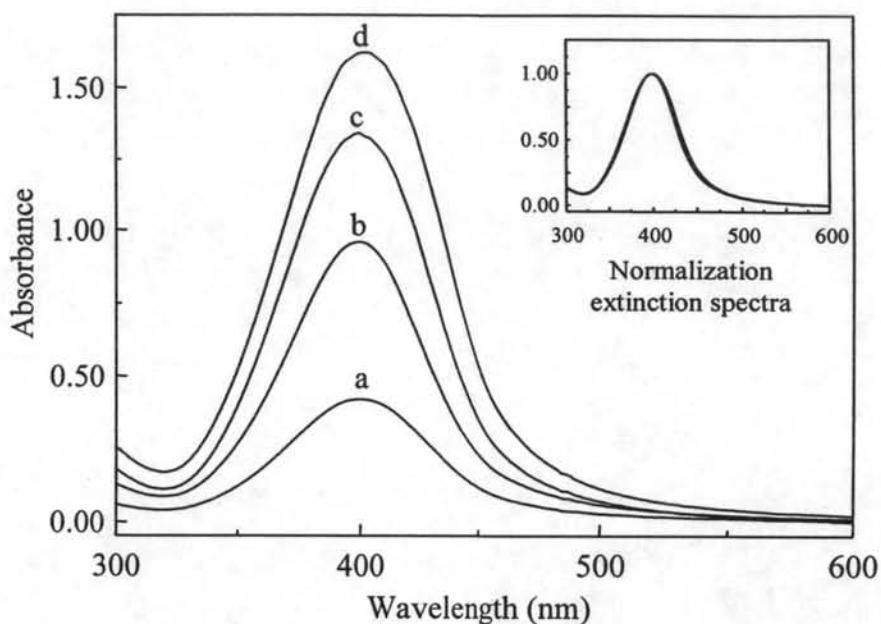


Figure 4.9 UV-Visible extinction spectra of synthesized silver nanoparticles at various concentration of silver nitrate: (a) = 0.3 mmol/L, (b) = 0.5 mmol/L, (c) = 0.7 mmol/L, (d) = 1 mmol/L. Normalized spectra are shown in the inset.

With increasing the concentration of silver nitrate, particle size should be increasing. However, from the normalization spectrum, extinction maxima and FWHM does not change. The intensity of the extinction spectra increase with the concentration. These results imply that the concentration of silver nitrate only affected the amount of silver nanoparticles but did not affect their size, size distribution and morphology. The particle occurring in one drop does not aggregate because it is stabilized by the by-product of the reducing agent (glucose) as shown in Figure 4.10.

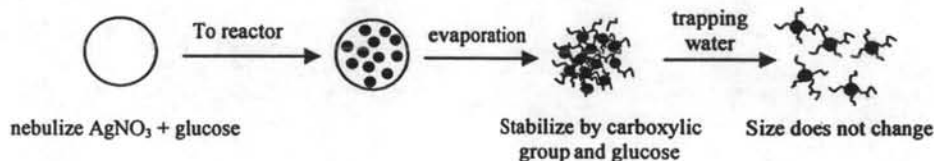


Figure 4.10 Proposed stabilizing mechanisms of silver nanoparticles.

When the concentration of silver nitrate was increased beyond 1.0 mmol/L, such as 1.5 mmol/L as shown in Figure 4.11, the formation of larger particles was observed as a black powder precipitated in trapped water. The UV-Visible extinction spectrum of synthesized silver nanoparticles also showed the absorption at longer wavelength and the baseline is shifted due to the light scattering by large silver particles. This result indicated that the reaction did not occur completely within droplet and the silver ions were left in trap water. Silver ion undergoes reduction or surface reduction on the pre-existing silver nanoparticles and aggregation to form large particles. Therefore, silver nitrate concentration was limited at 1.0 mmol/L.

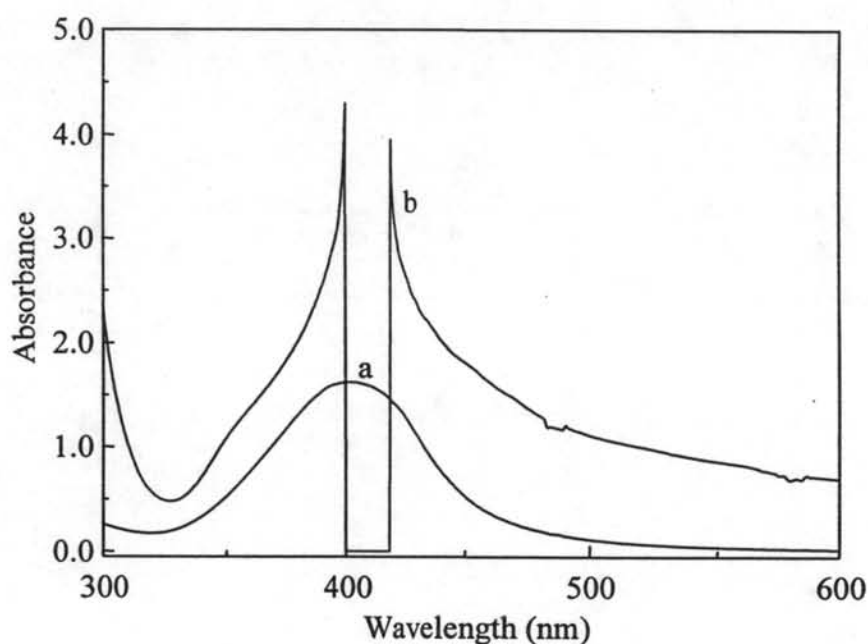


Figure 4.11 UV-Visible extinction spectra of synthesized silver nanoparticles with the silver nitrate concentration of (a) 1.0 mmol/L and (b) 1.5 mmol/L.

4.4.2 The concentration of glucose (reducing agent)

The concentration of glucose will affect the rate of the reaction in each droplet. When increasing the concentration of glucose, the reaction should occur more rapidly and more completely. The concentration of glucose was varied from 0.001 mol/L to 0.75 mol/L as shown in Figure 4.12.

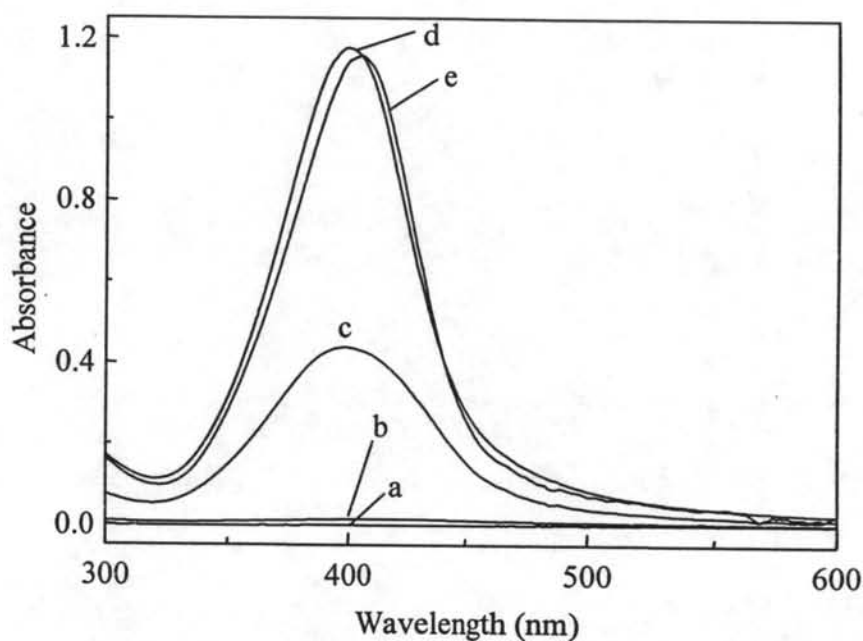


Figure 4.12 The UV-Visible extinction spectra of synthesized silver nanoparticles various concentration of glucose: (a) 0.001 mol/L, (b) 0.01 (mol/L), (c) 0.25 mol/L, (d) 0.5 mol/L, and (e) 0.75 mol/L.

When the concentration of glucose at 0.001 mol/L and 0.01 mol/L, silver nanoparticles did not observe in the trap water because of the low reaction rate. The minimum concentration that we observed the particle formation was 0.25 mol/L. If the concentration of glucose is increased higher than 0.5 mol/L, the red-shift in the UV-Visible extinction spectrum was observed. This indicates that there is the formation of the larger silver nanoparticles. This might come from the fact that the reaction occurs too early in nebulizer reservoir. This resulted in the formation of silver nanoparticles in the nebulizing droplet. The pre-existing silver nanoparticles undergo

surface reduction (autocatalytic) and cause the formation of larger silver nanoparticles as shown in Figure 4.13.

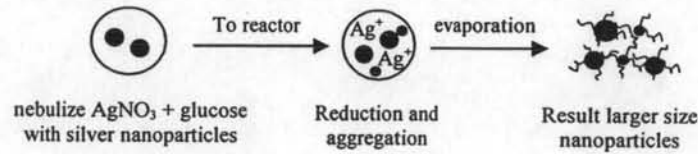


Figure 4.13 Schematic illustration of thermal reduction of sprayed silver method which have the silver nanoparticles in nebulizer reservoir.

In general, the mole ratio of the silver nitrate and glucose are 1:1 as shown in equation 4.1 but in the other literature [19], the mole ratio of silver nitrate:glucose about 1:10 were used because glucose is a weak reducing agent. In this study, the concentration of glucose is very high which the mole ratio about 1:100 were used because the residence time of droplet in tubular reactor is only 1-2 seconds.

4.4.3 The concentration of ammonia solution

The ammonia solution increases the rate of the reaction because formaldehyde and glucose are oxidized easier under basic conditions. The UV-Visible spectra of synthesized silver nanoparticles at various concentrations of ammonia solutions are shown in Figure 4.14.

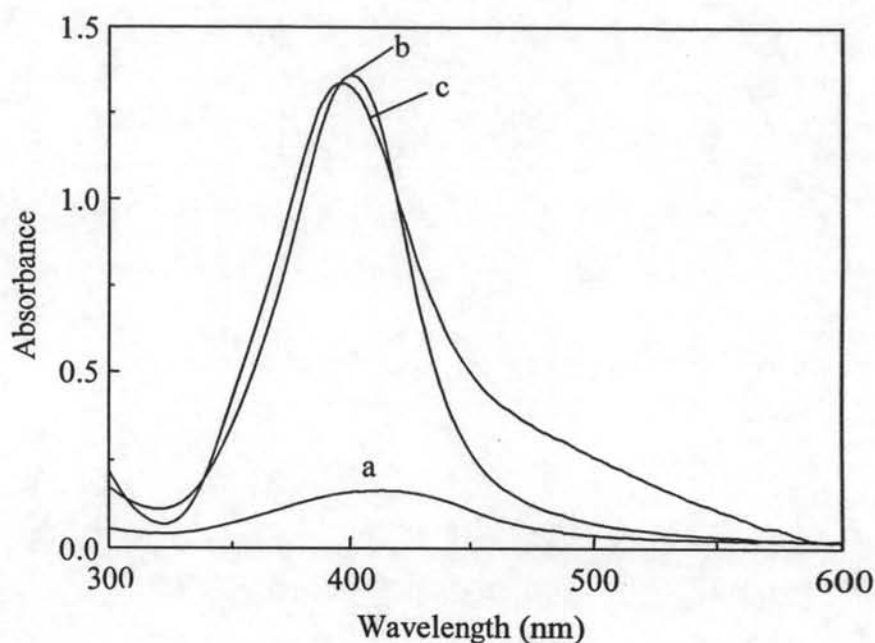


Figure 4.14 The UV-Visible extinction spectra of synthesized silver nanoparticles varied concentration of ammonia solution: (a) 0.0011 mol/L, (b) 0.0110 mol/L, and (c) 0.1100 mol/L.

The results were in analogy to the effect of concentration of glucose on the reaction rate. If the concentration of ammonium solution is too high, the reaction will occur in the nebulizer reservoir. So, the obtained silver nanoparticles were large as shown in the spectrum of 0.11 M of ammonia solution where an additional shoulder at about 500 nm was observed. This indicated that the spectrum consists of the broadened size and shape particles in the aggregated system.

4.4.4 Temperature in tubular reactor

Temperature in the tubular reactor also affects the rate of the reaction in the aerosol droplet. In this study, the reduction of silver ion should occur completely in order to prevent the reaction occurring in the trapped water which results in the large particle sizes. From our preliminary observation, the minimum temperature required was 60 °C in order to form nanoparticles from the precursor solution. However, the temperature in the tubular reactor was measured at the wall of the tube which was not the exact temperature in the tubular reactor. Generally, temperature in the tubular

reactor will decrease from the set point about 20 °C. Therefore, the temperature was varied from 80 to 200 °C in order to find the appropriate temperature in the thermal reduction of sprayed silver salt. The maximum temperature in tubular reactor was 200 °C because of the limitation of thermocouple. The UV-Visible extinction spectra of various temperatures are shown in Figure 4.15.

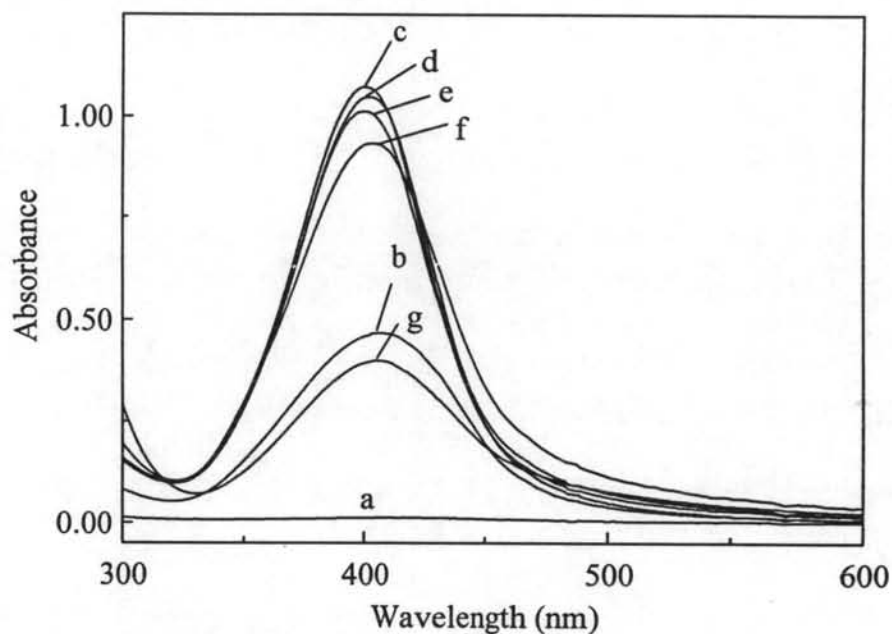


Figure 4.15 UV-Visible extinction spectra of synthesized silver nanoparticles of various temperatures in the tubular reactor: (a) 80°C, (b) 100°C, (c) 120°C, (d) 140°C, (e) 160 °C, (f) 180 °C, and (g) 200°C.

Plot of intensity at absorption maxima and peak area against temperature are shown in Figure 4.16.

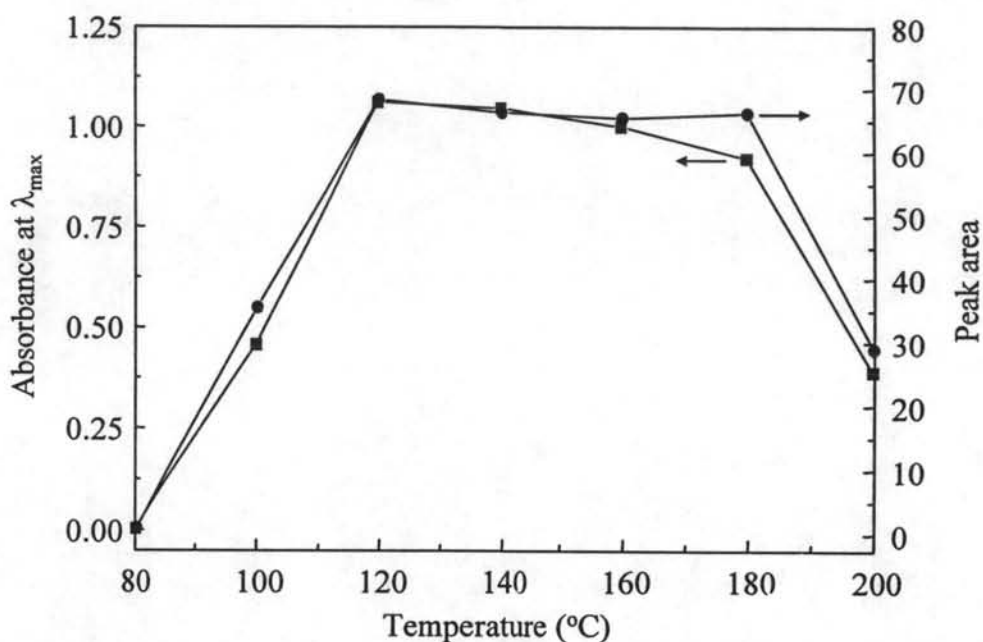


Figure 4.16 Plot of intensity at absorption maxima (—■—) and peak area (—●—) against temperature.

The results from the plot of intensity at absorption maxima against temperature are consistent with the plot of peak area against temperature except the plot at 180 °C. The peak area at 180 °C was higher because of the broadened peak which associated with the larger size of silver nanoparticles.

The intensity and peak area were increased as the temperature was increased. The maximum intensity was at 120 °C and began to decrease. In precursor heating method, the reaction was occurred at 60 °C. However, in this method even at 80 °C the reaction did not occur because the residence time of droplets in the tubular reactor was very fast. The reaction time was too low for reaction to occur at that temperature. When the temperature was 120 °C, the extinction spectrum has highest extinction maxima and highest peak area. At this temperature, the reaction was completed inside the reaction vessel. When temperature was higher than 180 °C, the reduction began to decrease because water evaporated and formed solid silver nitrate and solid glucose were formed which inhibit the reaction.

4.4.5 The flow-rate in nebulizer

Practically for the jet nebulizer, a higher gas flow, leads to the smaller output droplets. Here, the flow-rate was changed in order to study the effect of droplet size on the size of synthesized silver nanoparticles. However, the change of flow-rate also affects other factors such as residence time of droplets, temperature in the tubular reactor, and the trapping efficiency. The flow-rate was varied from 2.5 to 4.5 L/min. The UV-Visible extinction spectra of synthesized silver nanoparticles of various flow-rates were shown in Figure 4.17.

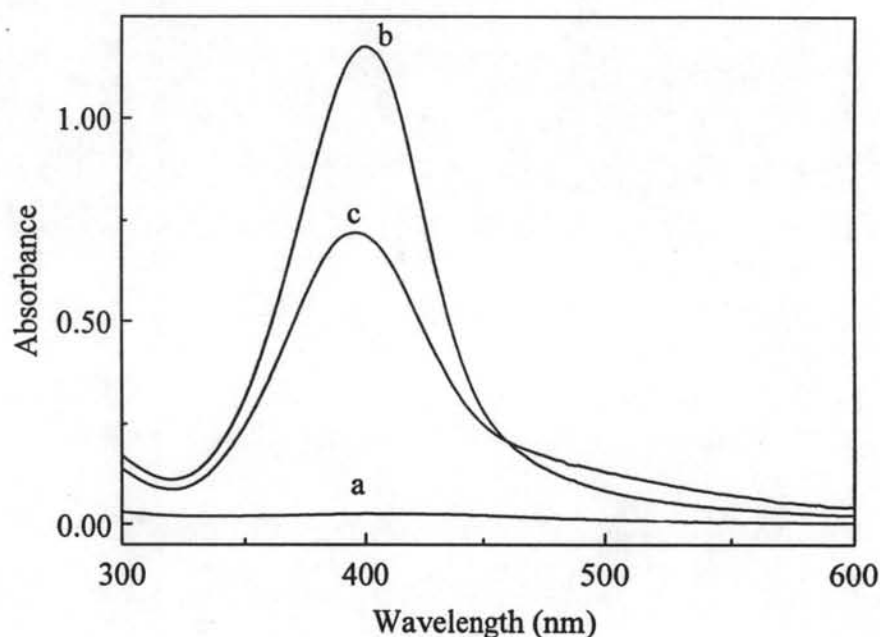


Figure 4.17 The UV-Visible extinction spectra of synthesized silver nanoparticles various flow-rates: (a) 4.5 L/min, (b) 3.5 L/min, and (c) 2.5 L/min.

Flow-rate of 4.5 L/min

The highest flow-rate yielded the smallest droplet, and the smallest silver nanoparticles should be obtained. However, from the UV-Visible spectrum in Figure 4.16(a) indicated that it did not have any silver nanoparticles in the trap water. At high flow-rate the resident times and trapping efficiency were decreased. As a result, the reduction did not occur due to the short resident time and temperature was too low or

the reduction occurred but the aerosol could not trap due to the flow-rate was too high.

Flow-rate of 3.5 L/min

At this flow-rate, we observed the UV-Visible extinction spectrum of the product at 400.27 nm and had the highest intensity. This indicated that the reaction completed in droplet and the synthesized silver nanoparticles were trapped in water.

Flow-rate of 2.5 L/min

This flow-rate has largest droplets and the largest silver nanoparticles could be obtained. It had the longest resident time in the tubular reactor, and has highest trapping efficiency. However, UV-Visible extinction spectrum shows that the lower intensity than at 3.5 L/min, tailing around 500 nm. This indicated that the synthesized silver nanoparticles were large. This result suggested that the droplets were probably struck in the tubular reactor or the droplet was too large and attached to the glass tube.

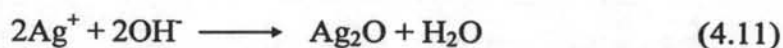
The optimum flow-rate in thermal reduction of sprayed silver salt method was about 3.5 L/min which suitable for trapping the aerosol, long resident times for completing the reaction, and smallest silver nanoparticles were obtained.

4.4.6 The type of carrier gas

In general, the synthesis methods for metal nanoparticles were used inert gas such as N₂ or Argon to purge out the oxygen that dissolved in the precursor solution. If the silver nanoparticles solution contains oxygen, it will oxidize silver nanoparticles into silver ion. The redox reaction can be written as follows:



The possible products of dissolution of silver particles may be silver oxide (Ag₂O):



In order to prevent the reversible reaction and the formation of silver oxide, N_2 was used instead of air. Before the reaction was carried out, nitrogen was flown in the nebulizer through tubular reactor for 3 min. The UV-Visible extinction spectrum of synthesized silver nanoparticles which purge N_2 was collect and compared with that air purge. The results are shown in Figure 4.18.

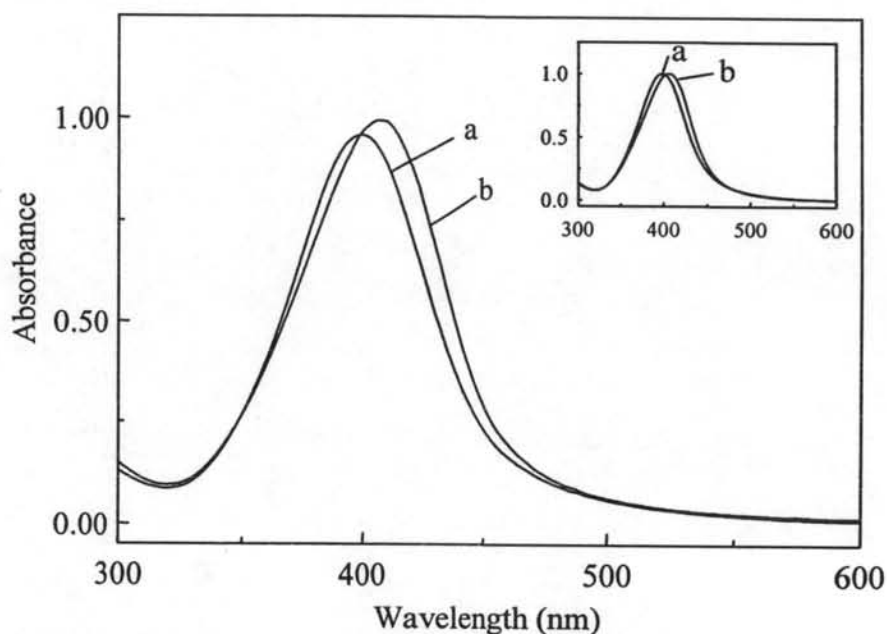


Figure 4.18 UV-Visible extinction spectra of synthesized silver nanoparticles under two different carrier gases: (a) air and (b) N_2 . Normalized spectra are shown in the inset.

The extinction spectra of synthesized silver nanoparticles using air and N_2 as carrier gas have the absorption maxima at 399.67 nm and 407.87 nm, respectively. This result indicated that the size of synthesized silver nanoparticles using N_2 were larger. When using air as carrier gas, smaller particles were obtained because the dissolution of silver nanoparticles in excess reducing environment. As a result, the silver ions which regenerate by oxygen were reduced by excess reducing agent to obtain smaller silver nanoparticles as shown in Figure 4.19.

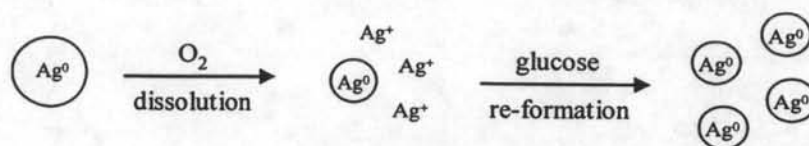


Figure 4.19 Schematic illustration of dissolution and re-formation of synthesized silver nanoparticles which result the smaller particles.

4.4.7 TEM images of synthesized silver nanoparticles by thermal reduction of sprayed silver salt method under an optimal condition.

TEM images of silver nanoparticles synthesized by thermal reduction of sprayed silver salt with optimum condition are shown in Figure 4.20. From the TEM images, the synthesized silver nanoparticles have spherical shape with diameter ranging from 10-20 nm which agreed with the UV-Visible extinction spectrum: extinction maxima at 400 nm indicated small size and FWHM about 58.05 nm indicated narrow size distribution.

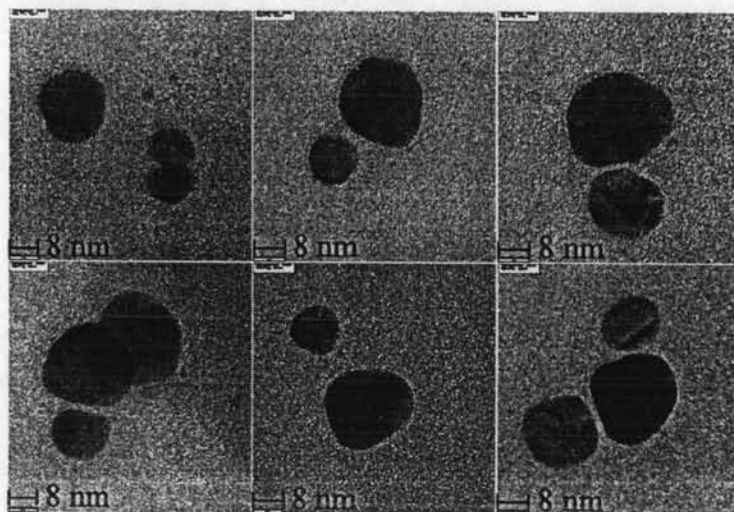


Figure 4.20 TEM images of synthesized silver nanoparticles by thermal reduction of sprayed silver salt under an optimal condition.

4.5 Comparison of thermal reduction of sprayed silver salt method, precursor injection method, and precursor heating method

The synthesis of silver nanoparticles by heating the precursor solution generally yields large particles with broad size distribution. In order to obtain the smaller and narrow size distribution silver nanoparticles, the rapid reduction and nucleation in a short period of time have to taken into account. Therefore, silver nitrate solution was added into hot reducing agent and maintained at the reaction temperature. This would produce a short burst nucleation and obtained smaller size and narrow size distribution. The UV-Visible extinction spectrum of synthesized silver nanoparticles by thermal reduction of sprayed silver salt was compared with the spectra of silver nanoparticles synthesized by precursor injection method and precursor heating method and the result are shown in Figure 4.21. Their corresponding photograph of synthesized silver nanoparticles by these methods was shown in Figure 4.22.

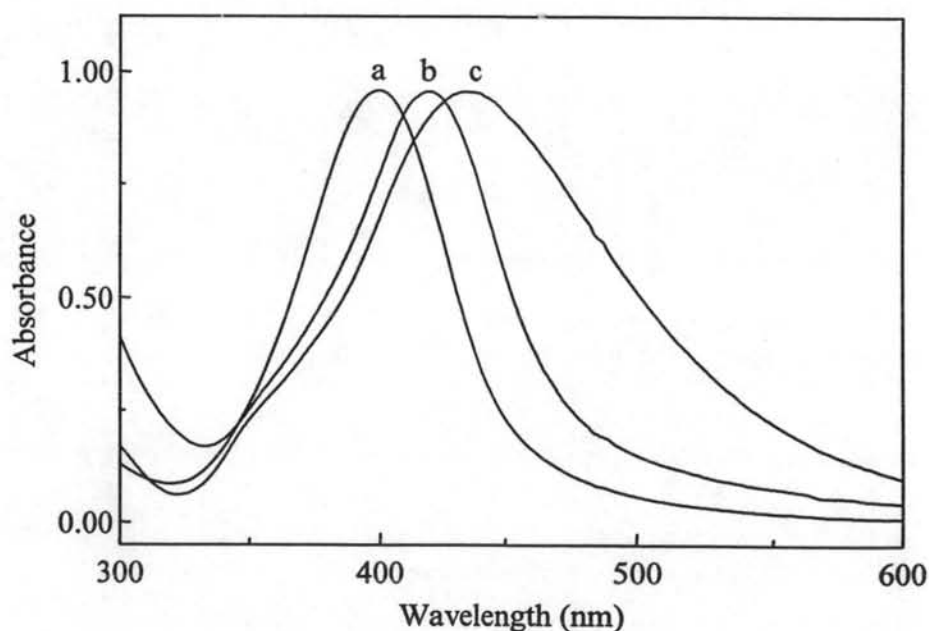


Figure 4.21 UV-Visible extinction spectra of synthesized silver nanoparticles by various synthesis methods: (a) thermal reduction of sprayed silver salt, (b) precursor injection, and (c) precursor heating method.



Figure 4.22 Photograph of synthesized silver nanoparticles by various synthesis methods: (a) thermal reduction of sprayed silver salt, (b) precursor injection, and (c) precursor heating method.

UV-Visible extinction spectrum of synthesized silver nanoparticles by thermal reduction of sprayed silver salt has extinction maximum at 399.26 nm and FWHM about 58.05 nm. For the UV-Visible extinction spectra of synthesized silver nanoparticles by precursor injection method and precursor heating method which have extinction maxima at 419.01 nm, and 433.12 nm and having FWHM about 67.42 nm and 115.72 nm respectively, indicate the larger size and broader size distribution than synthesized silver nanoparticles by thermal reduction of sprayed silver salt method.

The information in Figure 4.23 presents a schematic illustration of synthesis of silver nanoparticles methods: thermal reduction of sprayed silver salt method, precursor heating method, and precursor injection method. The differences of these methods are the size of reaction vessel and reduction rate of silver ion.

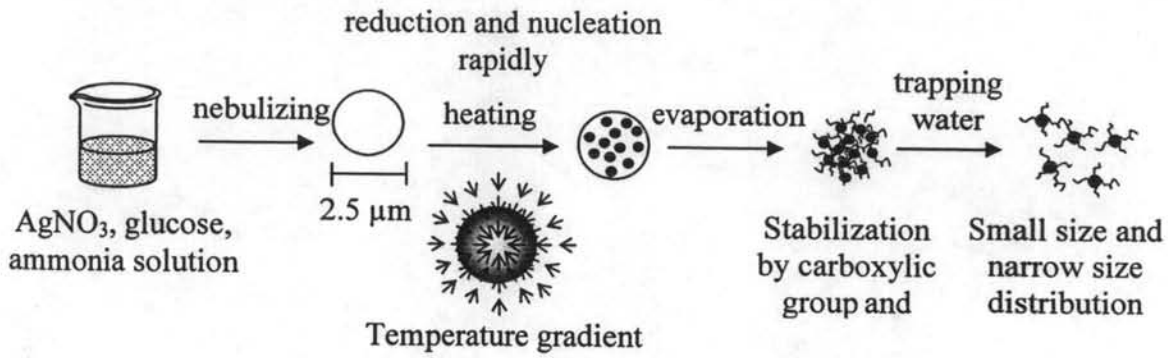
For thermal reduction of sprayed silver salt method, when silver salt and reducing agent were nebulized into tubular reactor, each droplet serves as a micro-reactor and the reaction occurs in each droplet. The temperature of the precursor increases very rapidly because the size of reaction vessel was very small. As a result, the reduction of silver ion proceeds very fast and converted all silver ion to silver nanoparticles which prevents the aggregation of silver nanoparticles by auto catalytic path way. Furthermore, the small reaction vessel affected the amount of silver ion species which limit the probability for nucleation, collision, and aggregation of

particles. The reaction time of this method was very short because the reaction occurred as the water in each droplets were evaporated which reduce nucleation and aggregation time. Therefore, the rapid reduction of silver ion, amount of silver ion, and short period of time for nucleation and aggregate of particles yield the synthesized silver nanoparticles that were small size and narrow size distribution.

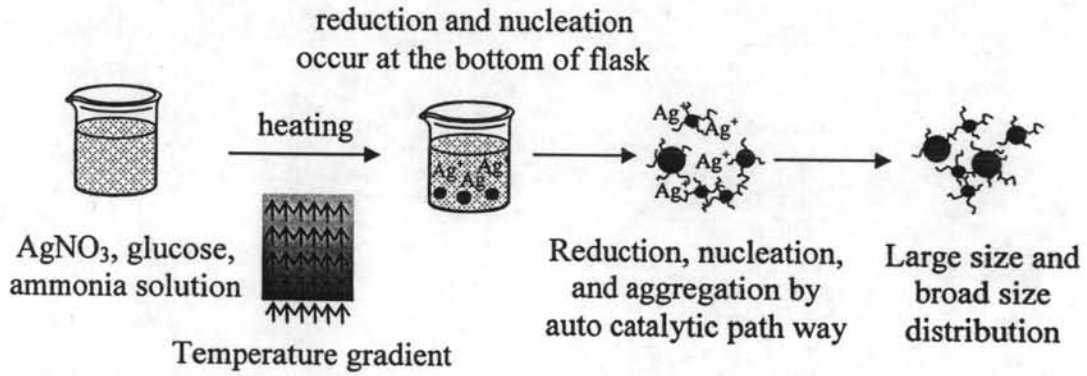
For the precursor heating method, when the precursor solution was heated, the temperature of the reactants gradually increased. Then, the reduction and nucleation proceed slowly at the bottom of beaker, some silver ion attaches on the surface of pre-existing silver nanoparticles and aggregation occur by auto catalytic pathway. Although, some silver ions were continuously reduced to silver nanoparticles. The long period of the reduction and nucleation step yielded the large particles size and broad size distribution.

For the precursor injection method, solution of silver ion was injected into the hot glucose solution resulting in the rapid reduction of silver ion to silver nanoparticles. Consequently, the nucleation occurred in a short period of time. Therefore, the nanoparticle size was smaller, and narrower size distribution was obtained compared to that of from precursor heating method. However, in this method involves the mixing of the injected silver ion solution and a reducing solution. The reduction was occurred at surface of droplet of injected silver ion solution while the internal of droplet still having the silver ion. As a result, silver ion in the solution could undergo reduction, nucleation, and aggregation by auto catalytic pathway. Moreover, the period of nucleation depends on the period of injection. Some pre-existing silver nanoparticles grew over a time that silver ion solution was continuously injected into a reducing agent. Therefore, particles size and size distribution of silver nanoparticles were larger than that obtaining from the thermal reduction of sprayed silver salt method.

Thermal reduction of sprayed silver salt:



Precursor heating method:



Precursor injection method:

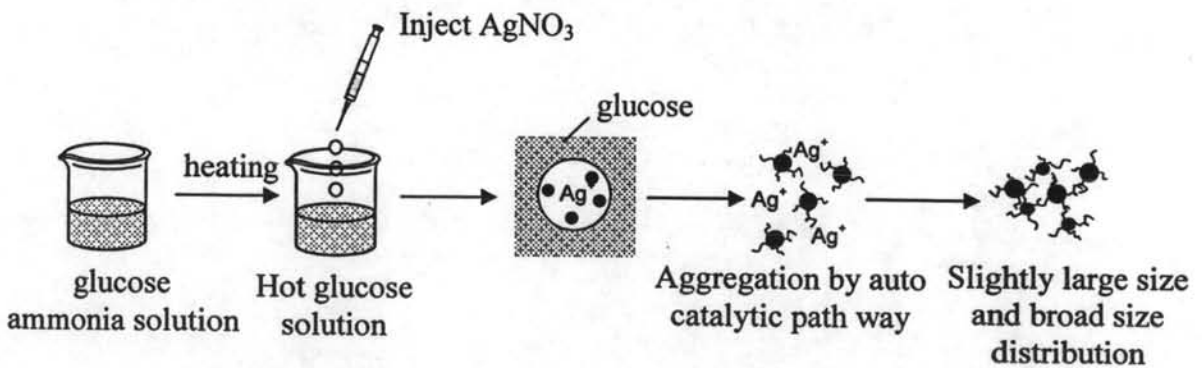



Figure 4.23 Schematic illustration of silver nanoparticles synthesis method: thermal reduction of sprayed silver salt, precursor heating, and precursor injection method (●: silver nanoparticles and : stabilized silver nanoparticles)

% yield

%yield can be calculated as follows:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \quad (4.12)$$

Actual yield

Silver nitrate concentration of 0.5 mmol/L 100 ml was used in order to obtain enough silver nanoparticles for measurement. The synthesized silver nanoparticles in trap water were centrifuged and washed with distilled water to remove all glucose and by-product. Then, they were dried by vacuum dry and the mass of synthesized silver nanoparticles was measured.

Weight of centrifuge tube	=	15557.0	mg
Weight of centrifuge tube + Ag ⁰	=	15560.4	mg
Weight of silver Ag ⁰	=	3.4	mg

Theoretical yield

$$\frac{g_{Ag^0}}{M_{Ag^0}} = \frac{[AgNO_3] \cdot V_{AgNO_3}}{1000} \quad (4.13)$$

$$\frac{g_{Ag^0}}{107.87} = \frac{0.5 \times 10^{-3} \times 100}{1000}$$

$$g_{Ag^0} = 5.3935$$

$$\% \text{ yield} = \frac{3.4}{5.3935} \times 100 = 63.03\%$$

%Yield of thermal reduction of sprayed silver salt method was 63.03% which compares to the chemical reduction method of 90% (if the reaction occurred completely). The lower yield might come from the fact that the aerosol product is hard to trap which observed during the experiment that the aerosol was leaked out from trap water. Moreover, droplets probably struck inside the wall of the tubular reactor.

4.6 Long-term stability of synthesized silver nanoparticles

Silver nanoparticles were generally unstable without using any stabilizer. When silver nanoparticles are kept for a long period of time, silver nanoparticles can aggregate and yield larger size and broad size distribution. This change can be monitored by observing the change in UV-Visible extinction spectrum.

The UV-Visible extinction spectra of synthesized silver nanoparticles were measured after synthesis, two weeks later, one month later and three months later as shown in Figure 4.24. The extinction spectra which measured after synthesis, two weeks and a month were found to have slightly changed in extinction maxima and FWHM but peak shape were not changed. Extinction spectra of synthesized silver nanoparticles after two weeks and one month were red-shift from 399.05 nm to 403.13 nm and 404.55 nm while FWHM were changed from 58.05 nm to 58.24 nm and 59.04 nm, respectively. Therefore, the size of synthesized silver nanoparticles was larger after prolong storage. However, the extinction spectra were red-shift only 4.08 and 5.50 nm. There were two reasons for explaining the stabilities of synthesized silver nanoparticles. (1) Silver nanoparticles were stabilized by carboxylic group as explained in section 4.3. (2) The reaction completely reduces all the silver ion species which prevents the surface reduction or the auto catalysis reduction on surface of silver nanoparticles. Therefore, the synthesized silver nanoparticles did not aggregate and formed larger particles.

An extinction spectrum of synthesized silver nanoparticles measured after three months significantly showed the change in extinction maxima. It was red-shift from 399.05 nm to 407.60 nm. The intensity of spectrum was decreased. This suggests that after storage silver nanoparticles for three months, silver nanoparticles was aggregated and form larger particles. The black powders in the storage vial were also observed as shown in Figure 4.25. This decreases silver nanoparticles in bulk water. So, the decreasing in the intensity of extinction spectrum after three months storage was observed.

Synthesized silver nanoparticles were stable for one month in refrigerator without adding any stabilizer. These results were important for industries because the stability of silver nanoparticles implied a long shelf life or service life-time of the products.

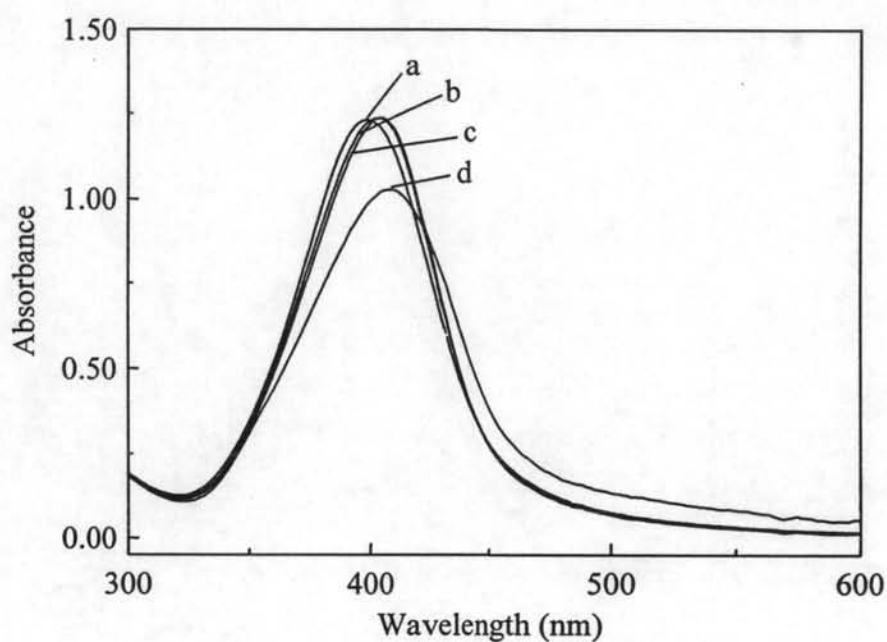


Figure 4.24 UV-Visible extinction spectra of synthesized silver nanoparticles which measured as a function of time: (a) after synthesis, (b) two weeks later, (c) one month later, and (d) three months later.



Figure 4.25 Photograph of synthesized silver nanoparticles in water after three months. Red circle show the black powder of silver nanoparticles.