Variable Frequency Microwave Synthesis of Silver Nanoparticles

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Abstract Synthesis of silver nanoparticles based on a polyol process and variable frequency microwave (VFM) was investigated. Comparing to a thermal method, the reaction by VFM radiation was much faster. The effects of silver nitrate concentration, poly(N-vinylpyrrolidone) (PVP) concentration, reaction time and reaction temperature were studied. It was found that the higher concentration of silver nitrate, longer reaction time and higher temperature increased the particle size while the higher concentration of PVP decreased the particle size.

Key Words: Variable frequency microwave, Silver nanoparticles, Particle size and distribution.

Introduction

Recently polymer nano composites have drawn much attention due to their unique thermal, electrical, mechanical and optical properties.[1] In particular, conductive nanoparticles such as silver and gold in a polymer matrix have shown a unique electrical property called Coulomb blockade,[2,3] which is beneficial for electronic

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device applications[3]. However, the dispersion of nanoparticles into a polymer matrix has been a bottle neck for nano composite fabrication. One of the best ways to uniformly disperse nanoparticles in a polymer is the *in situ* synthesis of the nanoparticles in a polymer matrix. In the current research, the silver nanoparticles were synthesized for the nano composite applications.

Many studies on silver nanoparticle synthesis have been conducted in recent years due to their unique properties in catalysis[4,5], electronics[6] and optics.[7] Usually chemical reduction methods were used to synthesize silver nanoparticles. Typical reducing agents include polyols,[8,9] $NaBH_4$,[10-12] N_2H_4,[13] sodium citrate,[14] and N,N-dimethyformamide,[15]. The polyol process is commonly used for preparation of easily reducible metals.[16] The polyols, such as ethylene glycol, diethylene glycol or a mixture of them, can act as the reducing agents as well as solvents in which the metal salts can be dissolved[9] or suspended[17]. In the polyol process, capping agents are used to protect nanoparticles from sintering with each other to form large particles. Poly(N-vinylpyrrolidone) (PVP) is one of the commonly used capping agents, which can passivate the surface of silver nanoparticles and prevent the possibility of silver-silver particle bond formation.[18]

Some of the chemical reducing reactions can be carried out at room temperature.[10,12] But most of them need elevated temperatures for a higher reaction rate. The energy used to heat up the media can be conventional thermal heating,[8,9] laser irradiation,[19,20] ultrasonic,[18] fixed frequency microwave radiation,[17,21] UV irradiation[22] etc. Microwave radiation is known to have a faster heating rate than the conventional heating through conduction and convection. Yanagida,[17] Komarneni[21] and Liu[23] have reported the use of a fixed frequency microwave (2.45 GHz) to synthesize platinum and silver nanoparticles. The microwave radiation heats up a material through its dielectric loss, which converts the radiation energy into thermal energy. The average power dissipated (P_{av}) by the material in the microwave field can be expressed as equation (1), in which ω is the applied angular frequency, E_{rms} is the electric field intensity, ε_0 is the permittivity of free space, ε''_{eff} is the effective dielectric loss factor of the material, and V is the volume of the material being heated. It can be seen from this equation that the higher the dielectric loss of a material, the higher the energy that can be absorbed. The penetration depth of a microwave is defined by equation (2), in which D_p is the depth of penetration of microwaves into the material, λ_0 is the wavelength of the microwaves, and ε' is the dielectric constant of the material. It can be seen that the penetration depth is proportional to the wavelength of applied microwave.

$$P_{av} = \omega \varepsilon_0 \varepsilon''_{eff} E_{rms}^2 V \quad (1)$$

$$D_p = \frac{\lambda_0 \left(\varepsilon'\right)^{1/2}}{\left(2\pi\varepsilon''_{eff}\right)} \quad (2)$$

Therefore, by varying frequency (wavelength) of the applied field, a microwave can penetrate a target material with different depths. Based on this principle, variable frequency microwave (VFM) was developed to heat up the material quickly and uniformly. VFM has been used for thermoset polymers[24] curing and Sn alloys soldering.[25] These studies have shown that the VFM heating provided faster and more uniform heating profile than the conventional thermal heating methods such as convection or conduction ovens.

In this paper, VFM synthesis of silver nanoparticles is discussed. It has been shown that using fixed frequency microwave radiation, fast reaction and narrow distribution of the nanoparticles can be achieved in comparison with the conventional heating methods.[19,20] Compared to the fixed frequency microwave, VFM provides more uniform heating, which can lead to a more homogenous nucleation. In addition, VFM can also heat metals without an arcing problem. The fast reaction rate of VFM method provides an important advantage for the *in situ* formation of nanoparticles in a thermosetting polymer, such as epoxy resin and polyester. In such cases, uniformly distributed nanoparticles must be formed prior to curing of the thermosetting polymers since nucleation and growth of nanoparticles could be hindered by crosslinking reaction. Therefore, a fast heating rate, uniform heating profile and precise temperature control are required. To achieve this requirement, a VFM synthetic method of siliver nanoparticles is proposed in this paper. The polyol process to synthesize silver nanoparticles by VFM radiation method was used. The reactions between a VFM method and a conventional heating method were compared. Effects of silver nitrate and PVP concentrations, reaction time and reaction temperature effect on particle size were also discussed.

Experimental

First, specified amount of silver nitrate (99+%, Aldrich) and PVP (1.0634 g, M_w = 55000, Aldrich.) were dissolved in 20 ml ethylene glycol (Fisher), respectively. The amount of PVP and silver nitrate are shown in Table 1. For microwave heating, a 3 ml silver nitrate solution and a 3 ml PVP solution were put into a 20 ml vial together and stirred at room temperature for one minute. The stirring bar was then removed and the solution was placed into the variable frequency microwave oven chamber (VFM, MicroCure 2100, Lamda Technologies Co.) to react for 1 min at 160 °C. The center frequency of the microwave, the bandwidth and the sweeping time were 6.425 GHz, 1.15 GHz and 0.1 sec., respectively. The sample temperature was monitored by a built-in thermocouple immersed in a solution. The ramping rate in this study was set at 2 °C/sec. The applied power was controlled via a temperature feedback module.

For a thermal reaction, a 3 ml silver nitrate solution and a 3 ml PVP solution were put into a 20 ml vial equipped with a magnetic stirring bar. Then the vial was put into a 160 °C oil bath to react for 5 min. The temperature of the solution was monitored using a thermometer. It took 3.5 to 4 min for the solution to reach the temperature of 160 °C with the above experiment conditions.

The UV-visible absorption behaviors for silver nanoparticle suspensions were recorded by using UV/vis spectrophotometer (Beckman DU 520 general purpose with 1 cm quartz). Transmission electron microscopy (TEM, Hitachi 100C TEM vender) was used to observe the nanoparticles synthesized. TEM samples were prepared by dispersing a few drops of silver colloid on a carbon film supported by the copper grids.

Results and Discussion

I. Comparison between VFM and conventional heating methods

Figure 1 shows a comparison of the UV-visible absorption of silver nanoparticles produced by VFM radiation and thermal heating, where the concentration of $AgNO_3$ and PVP, and the reaction temperature were the same. After the reaction, both the solutions were diluted to the same extent for the UV test. Absorbance of silver nanoparticle suspension produced by VFM radiation was much higher than that of thermal heating. Based on Beer’s law, a UV-vis absorbance is directly proportional to the path length and the concentration of the suspension. From the figure, we can conclude that the suspension by VFM has a higher concentration of Ag nanoparticles.

Table 1 summarized the results of particle size analysis for nano silver synthesized via both VFM radiation and conventional heating methods. The average diameter and relative standard deviation of particle sizes at different reaction conditions are shown in the table. Figures 2, 3 and 4 show the TEM images of silver nanoparticles which were synthesized by VFM radiation under different reaction conditions. It can be seen that with the increase of the concentration of silver nitrate and the reaction temperature, the average diameter of silver nanoparticles increases and the distribution becomes broader. Figure 5 shows the TEM image of silver nanoparticles which were synthesized at 160 °C for 5 min by the conventional heating method. Comparing these four pictures and the data in Table 1, it can be seen that the silver nanoparticles synthesized by VFM method have a narrow size distribution because the heating by VFM is more uniform. It has been known that keeping uniform temperature distribution and heating rate for the entire solution were two important factors to achieve narrow distribution of nanoparticles.[26] VFM can penetrate the reaction solution with different wavelength of the microwave to heat the whole solution quickly and uniformly. On the contrary, the conventional heating method heats a solution from the outside to inside slowly, due to the limited thermal conductivity of the reaction vehicle and the solution, leading to unevenness of heat conduction. From the above data and analysis, it is obvious that VFM radiation is very suitable for the preparation of narrowly dispersed nano-sized particles.

Much efforts have been made to study the chemical reactions by using the microwave radiation.[19,20] It has been well known that the microwave effect can be divided into two parts: thermal effect and non-thermal effect.[27,28] The thermal effect refers to the significant heating rate acceleration that can be achieved by microwave radiation. Not only the heating is faster through microwave radiation, but also the temperature distribution of the solution is more uniform. As such, this has led to the fast reaction rate and narrow size distribution of the Ag nanoparticles in the current study. The non-thermal effect relates to the inherent characteristics of microwaves other than the thermal effects. In our VFM experiment, it took about 1 min to reach the desired reaction temperature and another min at the temperature to synthesize the Ag nanoparticles. In the control experiment in an oil bath, it took about 3.5 to 4 min to reach the desired reaction temperature and another 1 to 1.5 min at this temperature to synthesize Ag nanoparticles. Comparing these two temperature profiles, we can conclude that the duration at high temperature for the thermal method was approximately the same as, if not longer than the VFM method. However, a much higher concentration of Ag nanoparticles was observed in the VFM experiment than that of the thermal experiment with comparable average particle size. Therefore, it is likely that the microwave radiation significantly promoted the nucleation of the nanoparticles without interfering considerably with the particle growth process.

II. Effect of the concentration of $AgNO_3$ *and PVP, reaction time and reaction temperature*

Figure 6 shows the UV-visible spectra of silver nanoparticles suspension produced with different concentrations of silver nitrate by the VFM radiation. We can see that with the increasing concentration of silver nitrate, there was a red shift in the absorption peak of the spectrum. It has long been known that the maximum absorbance peak will shift to longer wavelength (red shift) when the particle size becomes larger.[29] This result indicated that increasing concentrations of silver ion can promote the growth of silver nanoparticles and lead to increasing particle size. This can be further confirmed by the TEM results (Figures 2 and 4) and the data in Table 1. Huang *et al*[30] also found this phenomena when they prepared stable colloidal silver nanoparticles by reduction of silver nitrate with 254 nm UV light in the presence of PVP.

Figure 7 shows the UV-visible spectra of silver nanoparticles produced under different concentrations of PVP by VFM radiation. It can be seen that the higher the PVP concentration the lower the maximum absorbance wavelength, and therefore, the smaller the nanoparticles. It was also found by Pal on his gold nanoparticle synthesis that increasing concentrations of PVP limited the particle size through the restriction of particle growth.[31] The coordination of PVP through its nitrogen atom can provide the capping effect to limit the nanoparticle growing process.

The UV-visible spectra of silver nanoparticles produced under different reaction times by VFM radiation are shown in Figure 8. With increasing reaction time, there was a red shift of the absorption peak on the UV-visible spectrum. This was mainly due to the fact that the particles grew with time and that longer reaction time can also promote the particle aggregation to form larger particles, leading to a red shift of the absorption peak.[32]

The UV-visible spectra of silver nanoparticles produced under different reaction temperatures by VFM radiation are shown in Figure 9. The high reaction temperature resulted in a red shift of the absorption peak, indicating that the size of silver nanoparticles became larger with the increase of reaction temperature when all the other reaction conditions were the same. The result suggested that the growth of silver nanoparticles was enhanced with the increase of reaction temperature. This was also observed by Esumi when they synthesized silver nanoparticles by UV irradiation.[18]

The above results showed that the effects of time, temperature, and concentrations of reactant and capping agent on the particle size in VFM synthesis are similar to the effects in the conventional synthesis using thermal heating or UV irradiation. This suggests that the growth mechanism of the nanoparticles in VFM synthesis is not much different from that in other methods. However, the strong UV absorption of the nanoparticle suspension using VFM synthesis suggests that the microwave radiation significantly enhanced the nucleation process and therefore resulted in a high concentration of Ag nanoparticles. The mechanism is still under investigation.

Conclusion

Silver nanoparticles were synthesized by a reduction method where VFM radiation was used as a heating source. Comparing to a conventional heating method, VFM provided a much faster reaction, resulting in a higher concentration of Ag nanoparticles with the same temperature exposure and duration. Other conditions, such as the concentration of silver nitrate and PVP, reaction temperature and reaction time have effects on the size and distribution of the nanoparticles. The size of the particles increased with increasing the concentration of silver nitrate and with decreasing the concentration of PVP. Also longer reaction time and higher reaction temperature increased the size of silver nanoparticles. These effects of reaction conditions on the size and distribution of silver nanoparticles for both VFM reaction and conventional thermal reaction are almost the same. It can be concluded that VFM heating had a strong effect on the nucleation of the nanoparticles while it did not interfere with the particle growth in the current experiments. By using VFM synthesis method, higher yield and narrower distribution of Ag nanoparticles can be achieved. It can be seen that VFM is a novel technique for nanoparticles synthesis.

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References

1. Kim, J. Y.; Kim, M.; Kim, H. M.; Joo, J.; Choi, J. H. *Opt. Mater.* **2003**, *21*, 147.

2. Taleb, A.; Silly, F.; Gusev, A. O.; Charra, F.; Pileni, M. P. *Adv. Mater*. **2000**, *12*, 633.

3. Pothukuchi, S.; Li, Y.; Wong, C. P. *J. App. Polym. Sci*. **2004**, *93*, 1531.

4. Jana, N. R.; Sau, T. K.; Pal, T. *J. Phys. Chem. B* **1999**, *115*, 103.

5. Andrews, M. P.; Ozin, G. A. *J. Phys. Chem.* **1986**, *90*, 2929.

6. McConnell, W. P.; Novak, J. P.; Brousseau III, L. C.; Fuierer, R. R.; Tenent, R. C.; Feldheim, D. L. *J. Phys. Chem. B* **2000**, *104*, 8925.

7. Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. Science, 1997, 277, 1978.

8. Sun, Y. G.; Xia, Y. N. *Science* **2002**, *298*, 2176.

9. Sun, Y G.; Mayers, B.; Herricks, T.; Xia, Y. N. *Nano Lett.* **2003**, *3*, 955.

10. Mallin, M. P.; Murphy, C. J. *Nano Lett*. **2002**, *2*, 1235.

11.Petit, C.; Lixon, P.; Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 12974.

12. He, S. T.; Yao, J. N.; Jiang, P.; Shi, D. X.; Zhang, H. X.; Xie, S. S.; Pang, S. J.; Gao, H. J. *Langmuir* **2001**, *17*, 1571.

13. Pal, T.; Maity, D. S.; Ganguly, A. *Analyst* **1986**, *111*, 1413.

14. Link, S.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3529.

15. Pastoriza-Santos, I.; Liz-Marzan, L. M. *Langmuir* **2002**, *18*, 2888.

16. Fievet, F. et al. *MRS Bull* **1989**, *14*, 29.

17. Yamamoto, T.; Wada, Y.; Sakata, T.; Mori, H.; Goto, M.; Hibino, S.; Yanagida, S. *Chem. Lett.* **2004**, *33*, 158.

18. Carotenuto, G.; Pepe, G. P.; Nicolais, L. *Eur. Phys. J. B* **2000**, *16*, 11.

19. Chen, Y. H.; Yeh, C. S. *Chem. Commun.* **2001**, *4*, 371.

20. Treguer, M.; Cointet, C. de; Remita, H.; Khatouri, J.; Mostafavi, M.; Amblard, J.;

Belloni, J.; Keyzer, R. de *J. Phys. Chem. B* **1998**, *102*, 4310.

21. Komarneni, S.; Li, D. S.; Newalkar, B.; Katsuki, H.; Bhalla, A. S. *Langmuir* **2002**, *18*, 5959.

22. Itakura, T.; Torigoe, K.; Esumi, K. Langmuir 1995, 11, 4129.

23. Yu, W. Y.; Tu, W. X.; Liu, H. F. *Langmuir* **1999**, *15*, 6.

24. Fang, X. M.; Scola, D. A. *J. Polym. Part A: Polym. Chem.* **1999**, *37*, 4616.

25. Moon, K.; Li, Y.; Xu, J. W.; Wong, C. P. *IEEE Proceeding of the 54th Electronics Packaging Technology Conference* **2004**, *54*, 1989.

26. Fuelong, D. N.; Launikonis, A.; Sasse, W. H. F. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 571.

27 Galema, S. A. *Chem. Soc. Rev*. 1997, 26, 233.

28. Gedye, R. N.; Rank, W.; estaway, K. C. *Can. J. Chem*. 1991, 69, 706.

29. Heard, S. M.; Grieser, F.; Barraclough, C. G.; Sanders, V. J. *J. Colloid Interface Sci.* **1983**, *93*, 545.

30. Huang, H. H.; Ni, X. P.; Loy, G. L.; Chew, C. H.; Tan, K. L.; Loh, F. C.; Deng, J. F.; Xu, G. Q. *Langmuir* **1996**, *12*, 909.

31. Mandal. M.; Ghosh, S. K.; Kundu, S.; Esumi, K.; Pal, T. *Langmuir* **2002**, *18*, 7792.

32. Lisiecki, I.; Pileni, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 3887.

Table 1. Preparation of PVP-Stabilized Silver Nanoparticles by VFM Radiation and Conventional Thermal Heating.

No.	$AgNO_3$/PVP (g/g)	Average Diameter (nm)	Standard Deviation (nm)	Relative Standard Deviation
1	0.0267/0.5317	15.51	5.59	0.36
2	0.0267/0.5317	24.40	9.62	0.39
3	0.01335/0.5317	15.44	5.29	0.34
4	0.0267/0.5317	14.42	6.68	0.46

Nos.1-3 were prepared by VFM radiation method, 1 and 3 at 160 °C; 2 at 180 °C. No. 4 was prepared by conventional heating method at 160 °C.

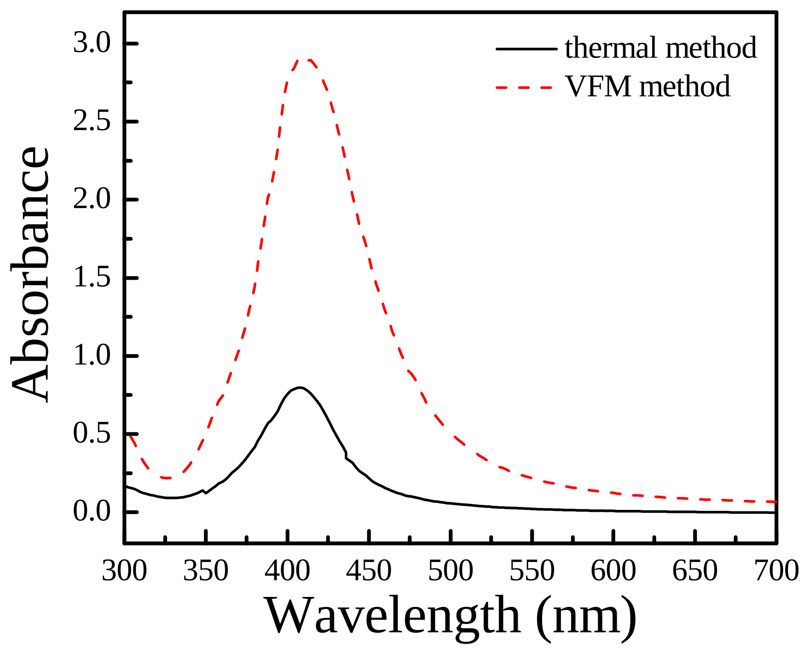

Figure 1. The UV-visible curves of silver nanoparticles produced by VFM radiation and thermal method at the same temperature of 160 °C for 5 min. The concentration of silver nitrate and PVP are the same.

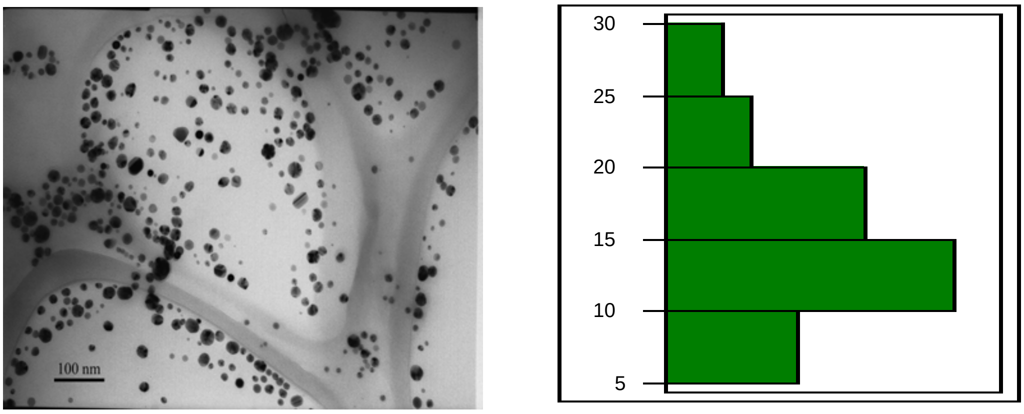

Figure 2. TEM micrographs for silver nanoparticles under the reaction of $AgNO_3$=0.0267 g in 20ml ethylene glycol, PVP=0.5317 g in 20 ml ethylene glycol at 160 °C by VFM radiation. The reaction time is 1 min.

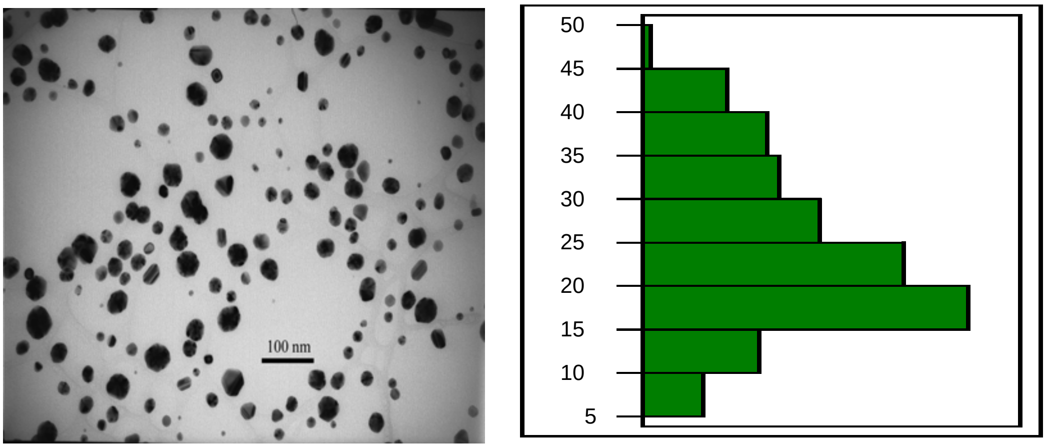

Figure 3. TEM micrographs for silver nanoparticles under the reaction of $AgNO_3$=0.0267 g in 20ml ethylene glycol, PVP=0.5317 g in 20 ml ethylene glycol at 180 °C by VFM radiation. The reaction time is 1 min.

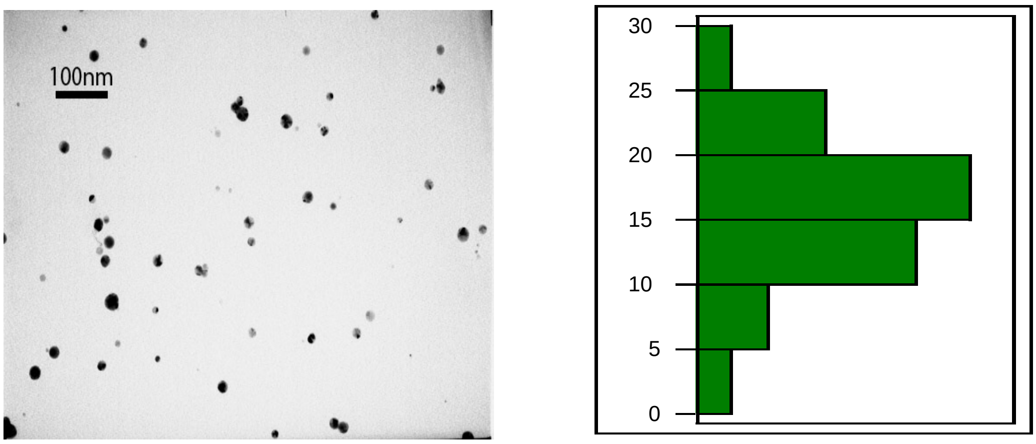

Figure 4. TEM micrographs for silver nanoparticles under the reaction of $AgNO_3$=0.01335 g in 20ml ethylene glycol, PVP=0.5317 g in 20 ml ethylene glycol at 160 °C by VFM radiation. The reaction time is 1 min.

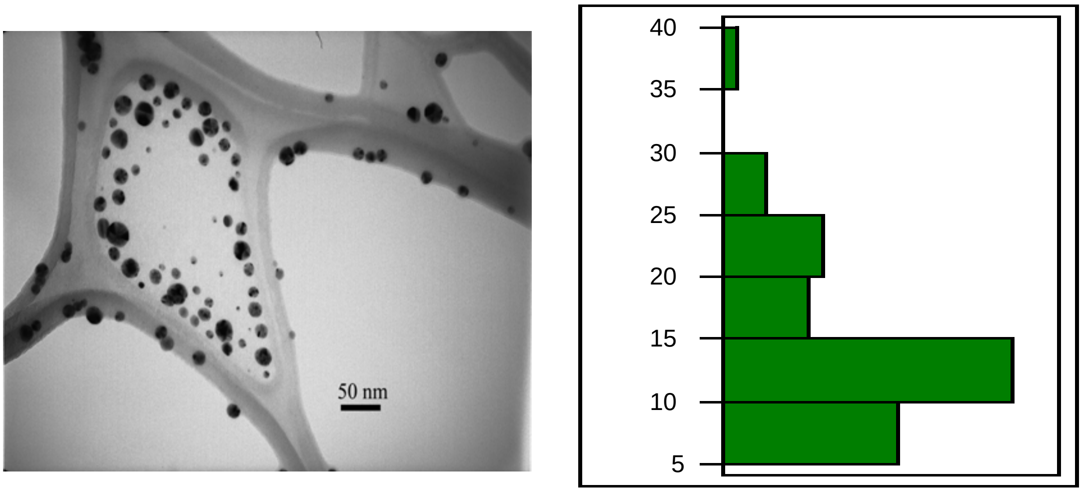

Figure 5. TEM micrographs for silver nanoparticles under the reaction of $AgNO_3$=0.0267 g in 20ml ethylene glycol, PVP=0.5317 g in 20 ml ethylene glycol at 160 °C by conventional thermal heating. The reaction time is 5 min.

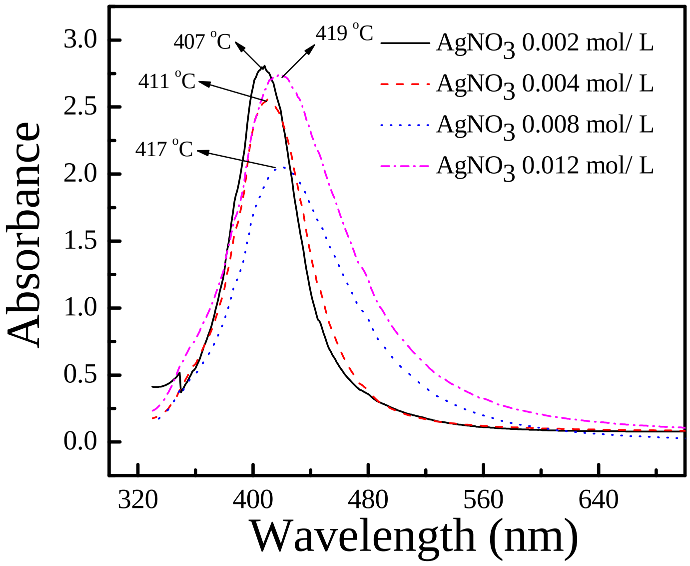

Figure 6. The UV-visible curves of silver nanoparticles produced under different concentrations of silver nitrate by VFM for 5 min at 160 °C. The concentration of PVP is the same

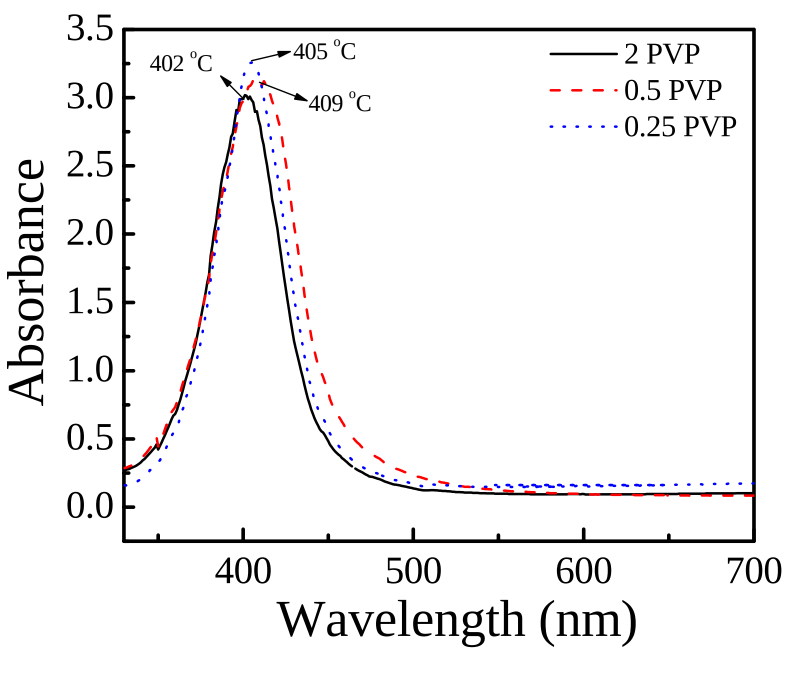

Figure 7. The UV-visible curves of silver nanoparticles produced under different concentrations of PVP by VFM for 1 min at 160 °C. The concentration of silver nitrate was the same.

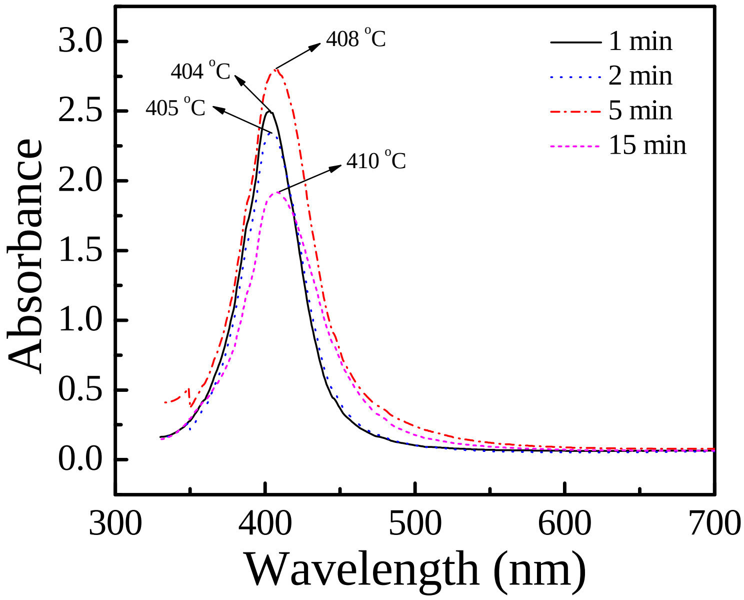

Figure 8. The UV-visible curves of silver nanoparticles produced under different reaction time by VFM at 160 °C. The other reaction conditions (concentration of silver nitrate and PVP) before the reaction are the same. After the reaction, the solutions were not diluted to the same extent.

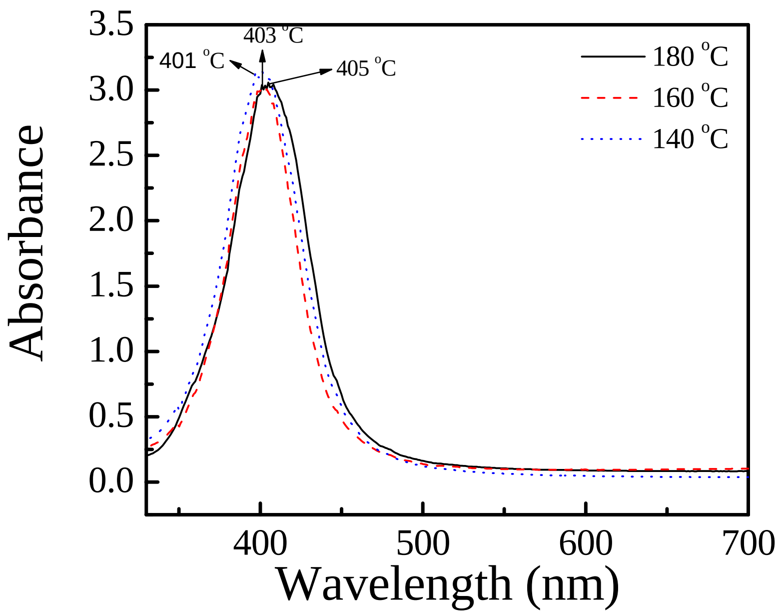

Figure 9. The UV-visible curves of silver nanoparticles produced under different reaction temperature by VFM for 1 min. The other reaction conditions (concentration of silver nitrate and PVP) are the same.