Influence of surfactant on the preparation of silver nanoparticles by polyol method

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Abstract
In this study, silver nanoparticles were synthesized from silver nitrate via a polyol method in ambient atmosphere. In our synthesis route, polyvinylpyrrolidone (PVP) is used as both size controller and capping agent, ethylene glycol acts both as solvent and reducing agent. The obtained silver nanoparticles were characterized by ultraviolet-visible spectrophotometry which indicated the formation of nanoparticles. Investigation of Fourier transform infrared spectroscopy clearly demonstrated the coordination between silver nanoparticles and PVP. Transmission electron microscopy (TEM) contributed to the particle size analysis. The surface plasmon resonance peak in absorption spectra of silver colloidal solution showed absorption from 406 to 409 nm. The average size of the resulting silver nanoparticles was below 10 nm with a dependency on the PVP concentration.

Keywords: silver nanoparticle, polyol synthesis, particle size control

Classification number: 4.02

1. Introduction
In recent years metal nanoparticles have been extensively studied because they now play an important role in many scientific and technological fields, from biology to materials science, electronics or mechanics [1–3]. Among the metal nanoparticles, silver nanoparticles have been widely investigated [4–6] because they exhibit unusual optical, electronic and chemical properties, depending on their size and shape, thus opening many possibilities for technological applications such as antibacterial, antistatic, cryogenic superconducting or biosensor materials. Currently developed synthesis methods for silver nanoparticles include chemical reduction [7, 8], polyol [9, 10], thermal decomposition [11], laser ablation [12], electron beam irradiation [13] and the in situ chemical synthetic route [14]. Among these methods, polyol synthesis was originally introduced by Fievet et al [15] as an excellent method for the synthesis of metal nanoparticles. Now the polyol method has become widely used by many research groups for the synthesis of metal nanostructures. In this work we used polyvinylpyrrolidone (PVP) as a protecting agent. Ethylene glycol acts as both reducing agent and solvent of silver nanoparticles. The purpose of this study is to synthesize size-controlled Ag nanoparticles that can be dispersed in solvent. We found that the amount of PVP used as dispersant is an important factor to control silver nanoparticles.

2. Experimental
All the chemicals were of analytical grade and used as purchased without further purification. Silver nitrate, AgNO₃ and ethylene glycol (EG) were purchased from Merck and Guangdong Guanghua Chemical Factory (China), respectively. Polyvinylpyrrolidone (PVP, average molecular weight of 40 000) from Merck, used as the capping agent, was dissolved in EG.

In a typical procedure, an appropriate amount of PVP was dissolved in 20 ml of EG. Next, AgNO₃ was added into the above solution. Then, an ultrasonic probe was immersed into the mixture solution for 3 min. After the start of the reaction,
the pale yellow solution changed to dark brown, indicating the formation of silver particles. The silver concentration in the synthesized solutions was 9.5 wt%. At this high concentration the solution is viscous and there is the necessity to dilute it for the various analyses. This was done in ethanol with a gentle ultrasonic dispersion (figure 1).

Synthesized samples were studied by ultraviolet-visible (UV-Vis) absorption spectroscopy from a double-beam spectrophotometer (Varian Cary 100) in the wavelength range from 190 to 1100 nm. Transmission electron microscopy (TEM) was used to study the particle size distribution. Drops of the suspensions were placed on a copper grid coated with carbon. Finally, Fourier transform infrared (FTIR) spectra were recorded (Brucker TENSOR 37 FT-IR spectrophotometer) between 400 and 4000 cm⁻¹ in solution.

3. Results and discussion

3.1. TEM photographs

According to [16,17], PVP plays a function of surfactant in the preparation of nanomaterials and of stabilizer of metal colloids. It was already shown [16–18] that the size and shape of nanomaterials strongly depend on the concentration of PVP. In this study, a constant silver nitrate concentration was used in EG solution. Concentration of PVP was varied from 0.001 to 0.006 M as shown in table 1.

The shape and size distribution of colloidal particles were characterized by transmission electron microscopy (TEM) 2 days after preparation. It is observed that the particles are nanosized and spherical. Figure 2(a) illustrates TEM image and the size distribution of colloidal silver particles for a PVP concentration of 0.001 M. With a size ranging from 18 to 132 nm those particles appear large and widely dispersed. As shown by the size distribution diagrams in figures 2(b) and (c), a slightly higher PVP concentration has a strong effect on the particle size. It appears that when a small amount of PVP is used, agglomeration occurs as a result of incomplete covering of the silver particles with PVP. Figure 2(b) displays the size distribution of colloidal silver particles for PVP concentration to 0.003 M, resulting in a smaller mean diameter of the nanoparticles (around 7 nm), as well as a much narrower distribution ranging from 3 to 12 nm. In this case it appears that the nanoparticles remain separate probably due to the fact that the surface of the silver particles is fully coated with PVP. When PVP concentration is greater than 0.003 M the particle size starts to increase again. As shown in figure 2(c), the size distribution of colloidal silver particles for a PVP concentration of 0.006 M shows a slightly greater mean diameter of the nanoparticles while maintaining a narrow distribution ranging from 4 to 16 nm. This indicates that excess PVP does not provide better coverage for the surface of the silver particles.

When increasing PVP concentration, the nucleation rate of the silver particles is much higher and the particle size decreases until an optimum is reached at 3 mM. This implies that PVP can prevent as-synthesized Ag nanoparticles from aggregating, producing smaller particles. Overall it clearly shows that the influence of the capping molecules' concentration is crucial to the control of mean diameter and particle size distribution of our silver nanoparticles.

3.2. UV-visible absorption spectra

The effect of PVP concentration on the formation of silver colloids was also studied by monitoring the UV-Vis absorption spectrum.

Figure 3 shows the UV-Vis spectra of silver colloids of the synthesized solutions. The peak positions are reported in table 1. As is clearly seen, the optical absorbance appears at a wavelength between 406 and 409 nm, which relates to the surface plasmon resonance of silver nanoparticles [19]. The peak position experiences a slight blue shift when increasing the PVP concentration from 0.001 to 0.006 M. The exact position of the plasmon absorption may depend on several factors (including particle size, shape, solvent type and capping agent) [19]. It would be expected that the distribution for 0.001 M PVP solution would be rather large above this wavelength but it might be that the agglomerated nanoparticles still form individual objects whose plasmon resonance is clearly determined. Even though we could not come to a clear observation of individual particles in this case, UV-Vis spectroscopy sustains the idea that even a small amount of PVP is sufficient to obtain silver nanoparticles.

3.3. Infrared spectra

EG is used to dissolve reactants as the main solvent. Figure 4 shows the FTIR spectra with or without nanoparticles. Coordination through ester bond of PVP to the silver is not come to a clear observation of individual particles. The peak position experiences a slight blue shift when increasing the PVP concentration from 0.001 to 0.006 M. The exact position of the plasmon absorption may depend on several factors (including particle size, shape, solvent type and capping agent) [19].
Figure 2. Transmission electron micrographs of Ag nanoparticles with variable concentration of PVP (0.001, 0.003 and 0.006 M) and their size distributions.

Figure 3. UV-Vis spectra of the different samples with varying PVP concentration.

the thin line spectrum in figure 4, the band at 1244 cm\(^{-1}\) corresponds to the absorption peak of the C=O bond. On the FTIR spectrum of PVP capped Ag nanoparticles with EG solution displayed by the thick line in figure 4, the band at 1244 cm\(^{-1}\) has disappeared. The band at 1400 cm\(^{-1}\) is related to the C–O bond. Our deduction is that PVP coordinates with
silver nanoparticles by breakup of $\text{C}==\text{O}$ double bond of the pyrrolidone groups.

The corresponding bonds clearly seem to be involved in the interaction with the silver nanoparticles. Further study is underway to understand their role and the possible way to engineer this coordination for controlling particle size over a wider range of mean diameter while keeping narrow size dispersion.

4. Conclusion

In summary, colloidal silver nanoparticles were synthesized successfully by a polyol method in EG solution. Silver nanoparticles synthesis is proved by the appearance of the surface plasmon resonance on these colloids. By varying PVP concentration, the size of particles could be changed. It was shown by TEM that the particle size decreases with increasing PVP concentration until a minimum, after which the particle size increases again. TEM observation also confirms that the particles are rather spherical and do not appear to be agglomerated in silver colloids. The smallest average diameter obtained is 7 nm. The PVP concentration has a remarkable effect on particle size and agglomeration of the produced nanoparticles.

Acknowledgments

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