Reduction of Silver Nitrate in Ethanol by Poly(N-vinylpyrrolidone)

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Abstract: Nanoparticles of silver have been prepared by reduction of silver ions in the presence of polymer. In particular, silver nanoparticles were prepared by reduction of silver nitrate in ethanol in the presence of chemical reduction and poly [N-vinylpyrrolidone (PVP)] as a protective agent. The UV-visible spectrum of the material shows a strong plasmon resonance band centered at 402 nm. The band position depends on PVP: silver nitrate weight ratios of silver colloids were influenced by the protective agent was absorbed to the particle surface. The rate constant remarkably depends in a first order on PVP : AgNO₃ weight ratios and reaction temperature.

Keywords: poly(N-vinylpyrrolidone), silver nitrate, reaction rate, nanoparticle size, particle size distribution

Introduction

Synthesis of silver nanoparticles is an area of considerable interest during the past decades [1-3]. The main applications of silver nanoparticles are found in catalysis and bactericide [4-6]. The most widely used constant material for the stabilization of silver nanoparticles is polymer such as poly [N-vinylpyrrolidone (PVP)] with metal nanoparticles. The PVP can also control the reduction rate of the silver ions and the aggregation process of metal atoms. The PVP control the aggregation of the silver atoms in solution. In practice, the reduction can take place after the interaction between the silver moieties and PVP. In this case, a complex between silver ions and PVP is formed, followed by the reduction the silver atoms on the PVP [7,8]. Recently, Kapoor and coworkers developed and optimized an effective technique for the preparation of dispersion of very small metal particles in the presence of PVP as a protecting agent [9,10]. Using PVP as a stabilizing agent, they managed to obtain stable dispersions of silver nanoparticles with an alcohol and ethylene glycol at reflux [11-16]. Liz-Marzan and coworkers showed that silver ions could be reduced in ethanol when certain surfactants were present and that the most efficient surfactant for the reduction was a nonionic ethoxylated surfactant [17,18]. It was shown that the reduction rate of silver ions is depends on the silver concentrations in the first-order.

In this work, stable colloidal silver has been prepared by reduction of silver nitrate as the reduction time with Ag⁺ ion concentrations, and reduction temperatures, in the presence of PVP. Examined here are the kinetic feature of the PVP as a protect agent of stable silver nanoparticles in ethanol. Its kinetics of forming the nanoparticles this method is suitable for studying the particle formation in situ by UV-visible spectroscopy. The UV-visible spectroscopy provides information on the formation kinetics as well as an indirect measure of the size and size distribution of the silver nanoparticles. With the use of different weight ratios of PVP/silver ions, influence of the PVP/silver ions weight ratios is examined. In addition, silver nanoparticles have been characterized by transmission electron microscopy (TEM) which is used for studying the size of the final silver particles and their morphology.

Experimental

Materials
Silver nitrate and poly(N-vinylpyrrolidone) (PVP, Mₜ = 40,000) were purchased form Aldrich. Ethanol was purchased from Fisher (99.9 %, HPLC grade). For the preparation of mixture solution, deionized water was used.

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Preparation of Metal Colloids
The silver sol was prepared by reduction of Ag⁺ ions using ethyl alcohol containing PVP was added. The weight ratios of metal salt to PVP were 1:5, 1:10, and 1:20. The solution was shaken and a clear yellow solution was obtained. The reducing temperature at 70 °C was performed in a thermostatic water bath. The time needed for completion of the reduction mainly depends on PVP contents and reduction temperature, and AgNO₃ concentrations ranging from 30 min to 24 h at reflux.

Experimental Techniques
UV-VIS absorption spectra of silver nanoparticles were measured in 1 cm optical quartz cuvettes using a Shimadzu 1650 UV-VIS double-beam spectrophotometer. The measurements were performed in a quartz cuvet at room temperature. Transmission electron microscopy (TEM) was performed with a Jeol JEM-2010 microscope; silver particle size distributions were calculated by image analysis, always over more than 100 counts.

Results and Discussion
On addition of silver salt to ethanol in the presence of stabilizer, the color of the solution changed from transparent to yellow. The color of the silver solution was found to depend on the concentration of the PVP and silver salt, and varied from bright yellow to dark yellow. The rate for the growth of Ag particles was found to depend on the ratio of PVP/AgNO₃. A typical variation of absorbance with time for 5 × 10⁻³ M AgNO₃ solution in ethanol is shown Figure 1. Only slight changes absorbance were detected during the first 5 min of reaction in the PVP : silver nitrate weight ratios of 5:1 and 10:1. At longer reaction times, the absorption band narrowed and shifted continuously to shorter wavelength. The evolution of the optical spectra was completed in about 9h in the PVP : metal salt weight ratio of 5:1. The shifts in the absorption band ceased after about 24 h, at which point a narrow and strong band centered at 400 nm was obtained, respectively. It showed that maximum optical density of early absorption band as well as of the final absorption band varied slightly, which of 20:1 after complete reduction was observed larger blue sift that of 5:1 and 10:1 as a function of PVP: Ag ion weight ratio.

The absorbance intensity vs. reaction time in the different PVP : AgNO₃ weight ratio is presented in Figure 2. The dependency on protecting agent can be observed. It comes out that the starting concentrations of PVP determine the maximum extent that the reduction can reach in each case. The reaction order can be from a plot differentiate data as a function of log absorbance intensity from Figure 2. First-order reaction was obtained from slope of results in all preparations [19]. The reaction rate constants, k is obtained by the integral method. The solid circles in Figure 2 are fit by first-order rate equation.

\[ A_t = A_\infty (1 - e^{-kt}) \] (1)

\[ -\ln(1 - a) = kt \] (2)
Where \( A_t \) is the absorbance at time \( t \), \( A_\infty \) the absorbance at a very long time \( (a = A_t/A_\infty) \), and \( k \) the first-order rate constant. The results of these fits are shown in Figure 3. As shown in these fits, \( -\ln(1 - a) \) is expected to linearly with time in simple first-order. The results of presented in Figure 3 (left) confirm this assumption since a straight line was obtained by plotting \( -\ln(1 - a) \) vs. time. Kinetics results were obtained \( k = 2.4 \times 10^{-4} \text{ min}^{-1}, k = 1.88 \times 10^{-3} \text{ min}^{-1}, 3.67 \times 10^{-3} \text{ min}^{-1}, \) and \( 1.72 \times 10^{-2} \text{ min}^{-1} \), respectively. The concentration of PVP is of relevance for the reaction rate. When a stabilizing agent such as PVP was added to form amide after addition of silver salt, stable dispersions of silver colloids were obtained. It shows the evolution of silver nanoparticles stabilized by PVP. On comparison with the results obtained in Figure 3 (right). In the presence of more amount of PVP, the rate of formation of silver particles increased drastically.

Figure 4 (left) shows absorption intensity as a reduction time of silver nanoparticles obtained at different silver nitrate concentrations in PVP. Kinetic traces showing formation of silver particles in PVP for different \( \text{Ag}^+ \) concentrations in the presence of constant PVP : \( \text{AgNO}_3 \) weight ratios. The dependence of reduction kinetics on the silver ions concentrations was observed \( 2.0 \times 10^{-3} \text{ M}, 3.0 \times 10^{-3} \text{ M}, 4.0 \times 10^{-3} \text{ M}, \) and \( 5.0 \times 10^{-3} \text{ M}. \) At concentration higher than \( 4.0 \times 10^{-3} \text{ M} \) the color of the colloids turned dark yellow. In all experiments plot of \( -\ln(1 - a) \) vs. time yielded solid line curves in Figure 4 (middle). In those cases, straight lines were obtained first order of the data. The slopes of the straight lines increased with increasing \( \text{AgNO}_3 \) concentrations. Kinetics results were obtained \( k = 8.21 \times 10^{-4} \text{ min}^{-1}, k = 1.13 \times 10^{-3} \text{ min}^{-1}, 1.34 \times 10^{-3} \text{ min}^{-1}, \) and \( 1.72 \times 10^{-2} \text{ min}^{-1} \), respectively. The observed rate constants varied linearly with silver nitrate concentrations. These results are showed in Figure 4 (right) and the slope of the straight line is \( 2.93 \text{ M}^{-1}\text{min}^{-1} \). The influence of temperature on the reaction rate was studied for initial concentrations \( 5 \times 10^{-3} \text{ M} \) in the PVP : silver nitrate weight ratios of 20:1. As shown in Figure 5, reaction rate increased with temperature. It seems that the maximum intensity was lower when the reaction was performed at higher temperature. First-order rate constants were obtained for these reactions by means of equation 2. Such constants are given in Figure 5 (left).
and plotted vs. the temperature. This plot shows that the rate constants follow Arrhenius’s law in Figure 5 (right). The activation energy calculated from fit was 3.72 kcal/mol, the reaction process can be promoted by a thermal mechanism.

The process of particle formation was also monitored by TEM, taking samples after 24 h. The particle size distribution of each sample was calculated by image analysis of 100 counts. A typical TEM image for a solution 5:1, 10:1, and 20:1 of PVP/AgNO₃ weight ratio is shown Figure 6 (right). The average sizes of nanoparticles in the presence of PVP/AgNO₃ ratios were found to be 5.6, 4.7,
and 3.2 nm. The reduction formation mechanism of PVP protected silver nanoparticles has been interpreted previously [16]. No clear trend was observed, but larger particles seemed to be formed during the first steps of the reaction, increasing afterward the proportion of smaller silver clusters [17]. PVP not only serves as both the coordinating agent and the stabilizing one, but also plays an important role in controlling the size and shape of metal nanoparticles. The hydrophilic amide groups of PVP are bound to the surface of metal particles due to the strong affinity of N and O atoms for transition metallic clusters, whereas the polyvinyl of PVP forms a hydrophobic domain, which surrounds metal particles and protects the particles from agglomeration [6]. The size distribution was more monodisperse silver particles in Figure 6 (right). As the reaction rate of silver particles increases with the concentration of PVP, it appears that this could be the reason for observing more regular for smaller particles and narrower particle size distributions at higher concentration of PVP.

Conclusions

Silver particles in the nanosize were synthesized in ethanol, by reduction of silver nitrate with PVP. The polyvinyl of PVP forms a hydrophobic domain, which surrounds metal particles and protects the particles from agglomeration. The reduction of silver ions in the presence of PVP leads to the formation of silver nanoparticles that are stable in solution.

The reducing rate is strongly influenced by weight fraction of PVP in the [PVP]/[AgNO₃] ratio, 20:1 weight ratio has drastically higher rate constant than obtained by 5:1. The rate constant remarkably increases with increasing [PVP]/[AgNO₃] weight ratio in the silver colloid, which implies easily reducible silver metals when an appropriate proportion of PVP is used. Mean diameter of silver nanoparticles decrease with increasing reaction rate. Protecting agent/metal ratio as well as reducing temperature is an important factor for narrow particle size distribution and smaller particle size in the silver nanoparticles.

References

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