

# Synthesis of highly concentrated silver nanoparticles

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## ABSTRACT

Two new preparation routes for the synthesis of highly concentrated Silver nanoparticles are presented here first. Silver nanoparticles were successfully synthesized in mild conditions using a high loading of silver acetate and water-soluble polymers as Poly-(vinylpyrrolidone) PVP, which was found here to act as both reducing and protecting agent. At the end of the reaction, after supernatant removal, highly concentrated silver nanoparticles (up to 40wt%) are obtained and characterized by TEM where 3-50 nm spherical silver nanoparticles can be observed. The second preparation route reported concerns the synthesis of highly concentrated silver nanoparticles (30wt%) in presence of polyethylene glycol and tert-butanol in mild conditions. The as-collected silver pastes were characterised by TEM and revealed spherical silver nanoparticles with 50nm particle sizes.

**Keywords:** wet-synthesis, emulsions, polymers, silver nanoparticles, high silver nanoparticles concentration.

## 1 INTRODUCTION

Silver nanoparticles are nowadays of great interest; either for their antibacterial properties or as a low temperature sintering conductive filler in electronic applications. In both cases, silver nanoparticles have to be optimally dispersed in a polymeric matrix while meeting stringent cost targets customary to such large volume markets. Current vapor phase processes are seen as highly investment-intensive leading to small chances of meeting cost targets, while recently published wet processes for silver nanoparticles suffer from drawbacks regarding cost effective large scale production. In some cases [1], the starting silver concentrations in the reactive medium are so low (0.06wt%) that large capacity reactors and time-consuming concentrations would have to be implemented. In other cases [2], the starting concentrations are satisfactory, but the proposed synthetic routes involve non-friendly organic solvents and reactants as toluene, phenylhydrazine and alkylamine. Tert-butanol is more of interest since it is a non-toxic product and could be used as solvent.

Compared to main reducing agents, as hydrazine, sodium borohydride and aldehyde, reported for the preparation of

silver nanoparticles, polyethylene glycol and polyvinylpyrrolidone are environmentally friendly products. For example, polymers of ethylene glycol are widely used in pharmaceutical and biomedical industries. polyvinylpyrrolidone (PVP) has been widely used as a surface passivation and stabilising agent in the synthesis of silver nanoparticles. [3,4] Although Silvert et al. observed the promoting effect of nucleation of PVP in the formation of silver particles using ethylene glycol as the reducing agent [5] there are few reports about the reducing properties of these 2 polymers for the fabrication of nanoparticles.[6] Recently, Luo et al. reported, for the first time, that polyethylene glycol is able to act as both reducing agent and stabilizer when used in the synthesis of silver nanoparticles in the absence of other chemicals. [1] In this case the maximum silver loading achieved is 0.12wt%.

Compared to the classical stabilising agents usually used, PEG and PVP are expected to show a weaker surface coordination to the silver nanoparticles, allowing a more active silver surface in device applications.

Herein, we report a new route to synthesize highly concentrated silver nanoparticles (30-40wt%) in mild conditions using aqueous solution containing PVP, as reducing and protecting agent, and silver acetate. We will also show that the addition of a reducing agent such as ascorbic acid, at the end of the reaction, doesn't seem necessary. We will also present a new synthetic route of highly concentrated silver nanoparticles using tert-butanol and PEG.

## 2 EXPERIMENTAL

### Synthesis of silver nanoparticles via the PVP process.

For a typical synthesis using PVP, 5 g of Polyvinylpyrrolidone (PVP) (MW 10000) was dissolved in 200 ml ultra-pure water at 50 °C under magnetic stirring. Then, 5g of Silver acetate (64.6 wt% Ag) was added to the solution at 50 °C. The mixture was kept during 45 minutes at 80 °C. Then, the mixture was left to cooling. At room temperature, a 20 mM ascorbic acid solution was added to the mixing under magnetic stirring. After 30 minutes reaction, the solution is kept without magnetic stirring, leading to a decantation. The supernatant is easily removed and the obtained silver paste is weighted. Ultra-

centrifugation was also performed on the mixing to extract the silver paste.

### Synthesis of silver nanoparticles via the PEG process.

For a typical synthesis using PEG, 1 g of polyethylene glycol (PEG) (MW 1500) was dissolved in 80 ml *tert*-butanol at 50 °C under magnetic stirring. Then, 10 g of silver acetate (64.6 wt% Ag) was added to the solution at 50 °C. The mixing was kept during 45 minutes at 80 °C.

Transmission Electron Microscopy (TEM) analyses of the particles were undertaken using a Philips CM200. Samples for TEM were prepared by placing a drop of the solution on carbon coated copper grid and dried at room temperature

## 3 RESULTS AND DISCUSSION

During the synthesis, color changes are observed showing the reduction process, and indicating the formation of silver nanoparticles. As soon as silver acetate is added into the yellowish PVP-water solution, the color turns from yellow to brown. At the end of the reaction, the color turns to dark green. After elimination of the supernatant, the silver paste has a content of 40 wt% silver. When the mixing is concentrated by ultra-centrifugation (2'000 rpm) the obtained silver content is higher than 45 wt%. The obtained dark green product was characterized by Transmission Electron Microscopy (TEM), as shown in Figure 1, where round shaped silver nanoparticles with particles size up to 50 nm can be observed. Observed colors changes clearly imply that PVP plays both the role of stabilizer and reducing agent in these synthesis conditions, whereas, in the literature it is mainly reported that PVP acts as a protecting agent in presence of a reducing agent [3,4].

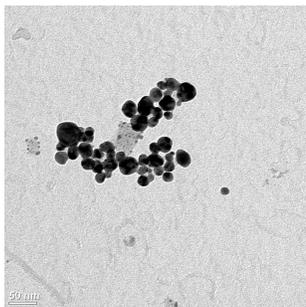


Figure 1: TEM pictures of 50nm Silver nanoparticles

The ascorbic acid (AA) is also used here as a reducing agent with the aim of finalising the reduction reaction. AA has a coordination affinity with  $Ag^+$ , while having a limited reduction potential preventing the agglomeration of the reduced silver nanoparticles. Thus, ascorbic acid can in a first step be linked to  $Ag^+$  ions in a stable way allowing the

electron transfer to occur on a second step. But in this case the addition of ascorbic acid didn't show a clear color modification. The color of the solution remained dark-green. But we could see as a first result that the TEM pictures shows particles of 2 to 25 nm. (figure 2A, 2B)

The same reaction results were obtained when replacing water by other solvents as *tert*-butanol and the reducing agent by PEG. The translucent PEG/*tert*-butanol solution turns from white to green color when silver acetate is added. At the end of the reduction process, particles of up to 50 nm are measured by TEM. To increase the silver concentration, a modified synthesis was realised with *tert*-butanol and PEG. Similarly to [1], we carried out experiments using PEG as both solvent and reducing agent. A silver loading of 9wt% maximum was achieved by this method, since the mixture became too viscous for easy manipulation. With the choice of *tert*-butanol as solvent, the silver loading achieved, at the beginning of the reaction, was of 16 wt% in the presence of PEG as reducing and protecting agent. A green color was observed at the end of the reaction showing that the reduction occurred. After elimination of the supernatant, a 30 wt% silver content in the silver paste is obtained. Round shaped particles are observed by TEM with sizes going up to 50 nm. (same as figure 1)

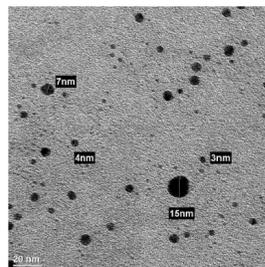


Figure 2A

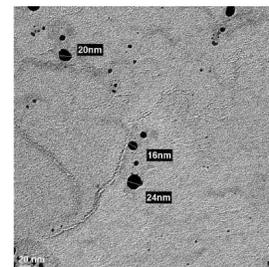


Figure 2B

Figure 2A and 2B: TEM pictures of 2 to 25 nm Silver nanoparticles

A study of the effect of silver concentration on the particles size synthesis was also carried out. As reported in table 1, we modified the silver concentration added at the beginning of the reaction from 1.5 wt% to 9 wt% silver, keeping the concentrations of PVP and PEG identical. The solvents used are water, and *tert*-butanol. As summarized in table 1, there is no color difference when a higher silver quantity is loaded for the same quantity of reducing agent probably indicating incomplete reduction. The silver nanoparticles sizes observed by TEM for the four products are all between 25 to 50 nm.

Products	1	2	3	4
Solvent	water	water	tert-butanol	tert-butanol
Reducing Agent	PVP	PVP	PEG	PEG
% Ag	1.5	9	7	9
Color of the product	dark green	dark green	green	green
Final wt % Ag	40	40	30	30
TEM (nm)	25-50	25-50	25-50	25-50

**Table 1. Conditions and Results for the synthesis of silver nanoparticles.**

For all the experiments, careful TEM examination did not reveal particles larger than 50 nm. They were not agglomerated, but effectively stabilised by the polymer. However, there are strong self-organising forces within the polymer-nanoparticle system. These interactions are demonstrated by TEM pictures performed on samples of silver paste which were diluted with 20 % of ethylene glycol/water (pictures 3A and 3B).

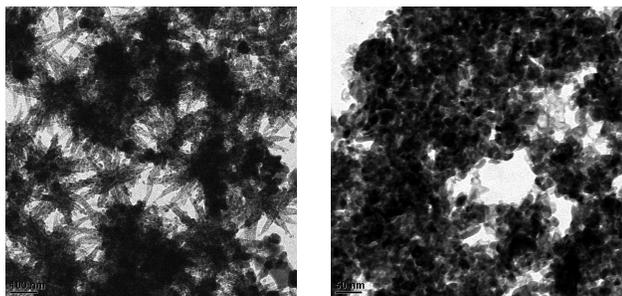


Figure 3A.

Figure 3B.

Figure 3A: Silver nanoparticles into the polymer matrix.

Figure 3B: is a magnification of Figure 3A.

## 4 CONCLUSION

Highly stable concentrated silver nanoparticles (above 40 wt%) were successfully prepared using mild synthetic conditions, under atmospheric pressure and friendly solvent without concentration step. In this procedure, PVP and PEG acted as both reducing agent and stabilizer for silver nanoparticles. Particles in the 2 to 50 nm size range can easily be produced in a one-step synthesis. Stability tests should be carried out in the future. Considering their ease of fabrication and active surface, such nanoparticles are expected to have wide applications in electronics and other related fields.

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