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SILVER MICRO-SIZED POWDER OBTAINED BY THE CHEMICAL REDUCTION

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Abstract

This paper presents the method for preparation the fine Ag powder with a particles size smaller than 2 μm. Reduction was performed from the nitrate solution directly by the vigorous stirring at the room temperature by the use of ascorbic acid as the reducing agent and polyvinylpyridine as the protecting agent. Silver powder with nearly spherical particles and size of micrometers were prepared by the chemical reduction and characterized by the scanning electron microscope (SEM). The SEM analysis has shown that preferred size, less than 2 μm was obtained. Silver with purity of 99.9% or more was obtained.

***Keywords**: silver powder, chemical reduction, polyvinylpyridine, ascorbic acid*

1 INTRODUCTION

Silver powder plays an important role in various applications. A coarse silverpowder is commonly used for the powder metallurgy processes, sintering of dissimilar materials and solder/braze pastes. It is usually in the range of size of 20 to 100 μm and granulometric composition of –200, –200 to +400 or –400 meshes. Common powder metallurgy methods like gas atomisation or electrolysis are used for the production of this type of the silver powder [1].

Fine and ultra-fine powders with the size from 100 nm to 10 μm have versatile application in the advanced industries. The use of ultra-fine powders includes: sensors, "high-end" of the solder type applications, batteries, catalysts, conductive coatings, inks and pastes, diamond tools, EMI/RFI shielding, masterbatch, sintering additives, electronic devices, and others [2,3].

In the few past decades, the synthesis of silver nanocrystals, particles ranging in size from 1 nm to 100 nm, has been intensively studied [4]. Nanoparticles (NPs) show the outstanding electrical, optical, magnetic, etc. properties that go beyond theirs in the solid state. Silver nanoparticles can be used as the antimicrobial agents and for electronic applications and different types of materials, like: antibacterial, antistatic, cryogenic, catalytic, superconducting and biosensor. Common synthesis methods of silver nanomaterials are the chemical reduction, photochemical method, ultrasonic-assisted reduction, electrochemical method, irradiating reduction, biochemical method, microemulsion method, ultrasonic spray pyrolysis, etc. [4–8].

Interest for the production of fine micro-sized silver powder (from 500 nm to 2.5 μm) is high, because it can be used in many applications where the nanoparticles are preferable but not required, like: electrically and thermally conductive pastes for usage in electronic and photovoltaics (solar cells), electrical contact alloys, solid oxide fuel cells, chemical catalysts, etc [9].

Many methods, such as the chemical reduction, photochemical or radiation chemical reduction, the sonochemical method, and the polyol method, are being applied currently to prepare the fine and ultrafine silver powders [9–11]. Various reducing agents are used for chemical reduction of silver(I) ions from aqueous $AgNO_3$ solutions. The commonly used reducing agents are: hydrazine hydrate, ascorbic acid, formal dehyde, trisodium citrate, glucose, K-Na-tartrate and hydroquinone in the presence of different protecting agents. Protecting agent, stabilizers or dispersants are usually the surfactants and common ones; polyvinylpyrrolidone (PVP), polyvinyl acetate (PVA), Dextran, various surfactants and some food industry additives like gelatin (E411), starch and gum arabic (E414) are also used [12–16].

In this paper, the silver particles were synthesized from the silver nitrate solution with ascorbic acid as a reducing agent and polyvinylpyrrolidone as a dispersant. The applied procedure was the same as in our previous studies [17,18], without a need for expensive equipment and with relatively low production costs.

2 EXPERIMENTAL

Scanning electron microscope model: JOEL JSM- 6610LV operated at 20 keV for determining the particle size and morphology of the silver powder were used. Chemical composition was determined using the Energy Dispersive X-ray Spectroscopy (EDS). The morphology of silver powder was studied using the SEM imaging.

The following chemicals were used for the silver reduction: silver nitrate p.a. (Merck, Germany), ascorbic acid p.a. (Merck, Germany), polyvinylpyrrolidone pharmaceutical (USP/Ph. Eur.) grade (Ashland/ISP, USA), Absolute ethanol p.a. (Zorka, Serbia) for silver powder rinsing was used. In the all experiments, the distilled water with conductivity lower than 2 μS/cm was used.

Analytical balance (Radwag AS 220.R2) with a maximum capacity of 220 g and d = 0.1 mg was used for measurement of chemicals. The pH of the electrolyte was monitored using a pH meter inoLab pH 720.

3 RESULTS AND DISCUSSION

In order to prevent the primary particles from assembling into larger particles during their growth stage, they should be protected by a suitable dispersant. It this research, the PVP K30 was used. It can be used in a combination with a surfactant. The all types of surface active agents are in use: anionic, cationic and nonionic. Although sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) and sodium lauryl ether sulfate ($CH_3(CH_2)_{11}(OCH_2CH_2)_nOSO_3Na$)

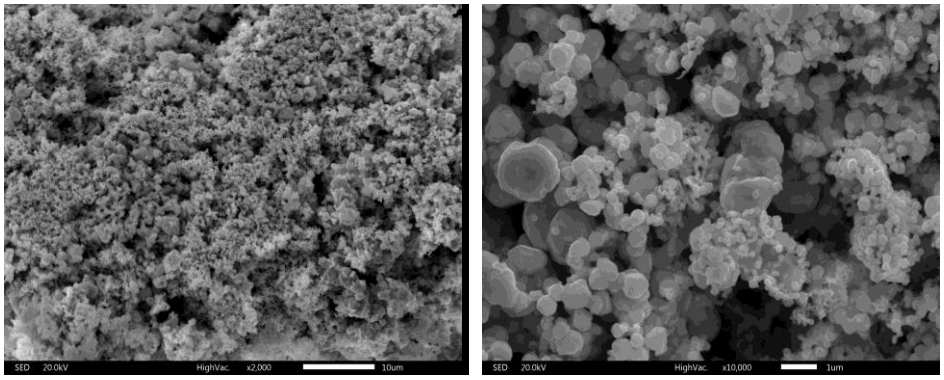
are commonly agents in a combination with PVP, a low solubility of silver sulfate should be considered.

It was found in this research that a relatively low concentration of silver nitrate and PVP with ratio of 1:1 to 1:2 is sufficient to achieve nearly spherical particles with a size of about a micrometer. Even the elevated temperature is not needed for the result.

Preparation of the silver micro-sized powder was performed by the use of 0.1M $AgNO_3$ solution as the source of the Ag^+ ions and 0.1M ascorbic acid solution as the reduction agent in both experiments. Protecting agent was PVP K30 and influence of its concentration was the main goal of the study. Total dispersant weight ratio of 1:1 and 2:1 to $AgNO_3$ equally divided in both solutions was tested. The corresponding concentration of PVP was 0.85 wt % in the solution of silver nitrate as well in the ascorbic acid solution in the first series of the experiments and in the second series was 1.7 wt % for the ratio of 2:1 (equal mass of PVP as silver nitrate in the both of used solutions). Reaction time was 30 minute in all experiments. Silver powder was filtered and rinsed with ethanol and warm (60 °C) distilled water.

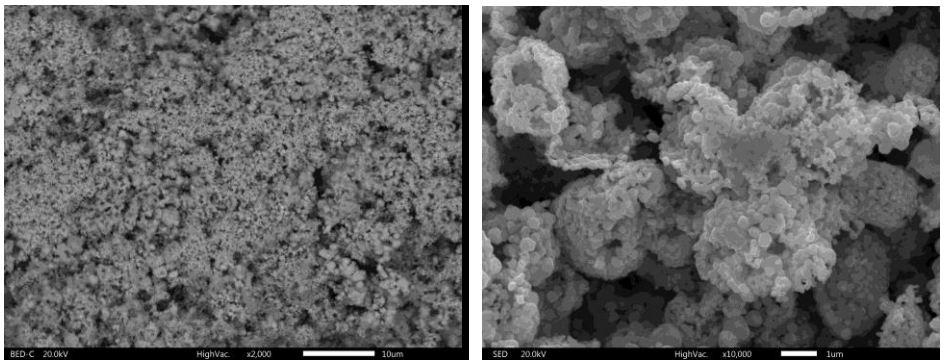
The results for the total weight ratio of PVP to silver nitrate 1:1 are presented in Figures 1 a) and b). Silver powder obtained in the same conditions except higher concentration of PVP K30 polymer, corresponding 2:1 weight ratio to the silver nitrate, is shown in Figures 2 a) and b).

Silver powders have more than 99.9% purity, determined by the EDS in all experiments.



Figures 1 *a) (left) and b) Silver powder obtained by the chemical reduction from 0.1M silver nitrate by 0.1M ascorbic acid in the presence of PVP K30 of 0.85 wt % in the both solutions*

It is obvious from Figures 1 a) and 2 a) that the similar results are obtained in the aim to get the particles smaller than 2 μm, but several larger particles in Figure 1 can be seen, even at a lower magnification.



Figures 2 *a) (left) and b) Silver powder obtained by the chemical reduction from 0.1M silver nitrate by 0.1M ascorbic acid in the presence of PVP K30 of 1.7 wt % in the both solutions*

Figure 1 b) reveals that despite the majority of particles are in the range of few hundreds of nm and some of primary about 100 nm, the agglomeration has already made the numerous stable particles with the size greater than a micro meter. Higher concentration of PVP produce agglomerates with size 2 to 4 μm that can be easily disintegrated by the prolonged use of ultra-sonic bath in the appropriate solvent. Shorter time and/or prolonged flushing of the powder also can defragment loosely bound clusters. In that case, instead of filtering, the centrifugation should be used for the silver powder recovery from the solution. Nearly spherical particles are obtained in both experiments.

4 CONCLUSION

Test of the technology for micro sized silver powder and influence of dispersant (PVP K30) concentration and ratio to the silver are investigated in this paper. It was shown that the same quantity of protecting agent as silver nitrate is not sufficiently to prevent against agglomeration of the stable particles larger than one micro meter for the time needed for total transformation, 30 min. Optimal ratio of dispersant to silver nitrate for the condition in the study is found to be 2:1. Reaction path, under required conditions and independently of the ratio of protecting agent, produces the spherical particles. Simplicity suggests the potential improvements of the process economy.

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