SINTEZA SREBRNIH ČESTICA VELIČINE MIKROMETRA PRIMENJIVE ZA DEBELO FILMNE KONTAKTE NA SOLARNIM ĆELIJAMA

SYNTHESIS OF MICRO-SIZED SILVER PARTICLES SUITABLE FOR THICK FILM CONTACTS ON SOLAR CELLS

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Glavni cilj studije bio je utvrditi parametre za proizvodnju srebrnog praha veličine oko jednog mikrometra, koji se može primeniti na paste koje se koriste u proizvodnji i održavanju solarnih ćelija. U svim eksperimentima korišćeni su rastvor srebro nitrata i askorbinske kiseline, kao izvor srebra, odnosno redukciono sredstvo. Polivinilpirolidon (PVP) i želatin su korišćeni kao disperzanti. Disperzant u ovom sistemu deluje kao zaštitno sredstvo na način da sprečava procese aglomeracije i agregacije. Uticaj korišćenih agenasa bio je različit, a jedan od ciljeva istraživanja bio je utvrditi njihove prednosti i nedostatke. Optimalni parametri sinteze bili su: temperatura rastvora od 45 °C, pH=7, koncentracija srebra i askorbinske kiseline od 45 g/l, odnosno 30 g/l. Iako se PVP pokazao pogodnim zaštitnim sredstvom za ciljeve studije, najbolji rezultati su dobijeni upotrebom želatina kao disperzanta u odnosu koncentracije prema srebrnim jonima od 2,5 mas. %.

Ključne reči:*srebro; pasta; električni kontakti; solarne ćelije; debeli filmovi.*

The main goal of the study was to determine parameters for the production of the micro-sized silver powder applicable to the pastes that are in use in solar cell production and maintenance. In all experiments, silver nitrate solution and ascorbic acid were used, as a silver source and reducing agent, respectively. Polyvinylpyrrolidone and gelatine were used as dispersants. The dispersant in this system acts as a protective agent in a way that prevents agglomeration and aggregation processes. The influence of used agents was different, and one of the aims in the research was to determine the pros and cons of them. The optimal parameters of the synthesis were the solution temperature of 45 °C, pH=7, and concentrations of silver and ascorbic acid of 45 g/l and 30 g/l, respectively. Although PVP has proved to be a suitable protecting agent for the goals of the study, the best results were obtained with the use of gelatine as a dispersant in the concentration ratio against the silver ions of 2.5 wt. %.

Key words: *silver; past; electrical contacts; solar cells; thick films.*

1 Introduction

Silver is used through a long history as a precious metal, mostly for the production of coins and for artistic purposes. It has extraordinary properties such as the highest electrical and thermal conductivity of all metals [1]. Silver also has excellent ductility, malleability, as well as, optical and antimicrobial properties [2, 3]. These characteristics have led to the wide use of silver in various industries, in the electronics, in the energy sector, for optics and medicine applications, in the environmental sector, like a catalyst in the chemical industry, and many others [4-6].

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Silver nanoparticles and nanostructures have been studied intensively in the last few decades due to their exceptional physico-chemical properties that are conditional and determined by their unique interfacial effects [7]. This provides very special applications in many fields of applied science such as biotechnology (biosensors, pest & microbial control, biosynthesis, pharmaceutical industry, etc.), special catalysis processes, photonics, photovoltaic devices, biofuels, lithium batteries and similar [8-10].

In the present time, a large number of the synthesis methods, for AgNPs (silver nanoparticles) obtaining, are developed. The most important of them are chemical reduction, use of gamma-rays, laser-assisted processes, electrochemical procedures, photochemical reduction, template method, and various biosynthesis [11-14]. Chemical reduction with the support of the polymer systems is still the simplest but very effective method, with low costs and excellent control of the particle size [15]. Aggregation processes can be hindered by stabilization and protection with the interpolyelectrolyte complexes [16].

Conductive inks and pastes, with the use of AgNPs, are used for printed and flexible electronics and front contacts of the crystalline silicon solar cells [17-18]. However, nanotechnology is not exclusive for this kind of application, and the silver powder with the particle size of 500-1500 nm has been extensively used for them [19, 20]. The aim of the paper is to establish maximal concentration of the reagents for the wet chemical reduction synthesis of the microsized silver powder in goal to achieve the most enonomic process for use in small and medium industry conditions. Additional aim was to get near spheric particles with small dispersion of their sizes and use that fine powder for the tick film in the solar energy applications.

2 Experimental

The following chemicals were used in the experiments: silver nitrate (extra pure, ≥99%, Chimet S.p.A., Italy), L-Ascorbic acid (p.a. grade, Kemika, Croatia), polyvinylpyrrolidone, PVP type K30 (pharmaceutical grade; Ashland, Nederland), gelatin (pharmaceutical grade; Institute Torlak, Serbia). Auxiliary reagents were citric acid monohydrate (for analysis, Carlo Erba Reagents, Italy) and sodium hydroxide (for analysis, ≥99%, Merck, Germany) for pH regulation and absolute ethanol (pro analysi, Zorka Pharma, Serbia) in the aim of silver powder rinsing. Double distilled water, with conductivity ≤ 1 μS/cm (ISO 3696:1987, Grade 2), was used for solution preparation and the single distilled water with conductivity ≤ 5 μS/cm (the same standard, Grade 3) for rinsing of the obtained silver powders.

The procedure in the experiments consisted of the following: two solutions were made separately, solution 1 was the solution of $AgNO_3$, and solution 2 was the solution of ascorbic acid (AA). The dispersant was equally divided into both solutions. Solution 1 has been added to solution 2 with continuous stirring. The temperature for the synthesis was 44-46 °C. In the experiments without pH corrections for the system, the total pH of the system was 3.4-3.7. Higher pH values were obtained by the use of 10% NaOH. Citric acid has been used only for fine-tuning of the pH. The exact pH values and concentration of reagents in the experiments are noted in the further text.

Scanning electron microscope (SEM) images and electron diffraction spectroscopy (EDS) analysis were performed on a JSM IT 300LV (JEOL, Japan) operated at 20 keV and an X-max (Oxford Instruments, UK), respectively. The particle size distribution was measured and analyzed using a Malvern Mastersizer 2000 and software Version 5.1 (Malvern Instruments, UK). The pH values of the solutions were measured by HI 991301 pH/EC/TDS meter (Hanna Instruments, Romania).

3 Results and disscussion

The silver powder obtained by classical chemical reduction of Ag+ ions with ascorbic acid in the presence of PVP polymer without pH adjustment was the referent material for comparison with the other more advanced procedures. This operation was the simplified industrial process and studied in previous research of the team [21]. Concentrations of the reagents were 45 g/L for Ag(I) ions, 30 g/L for ascorbic acid, and 10 g/L (approximately 1% wt.) for PVP. The reaction duration was 45 minutes, and the realized powder is in figure 1.

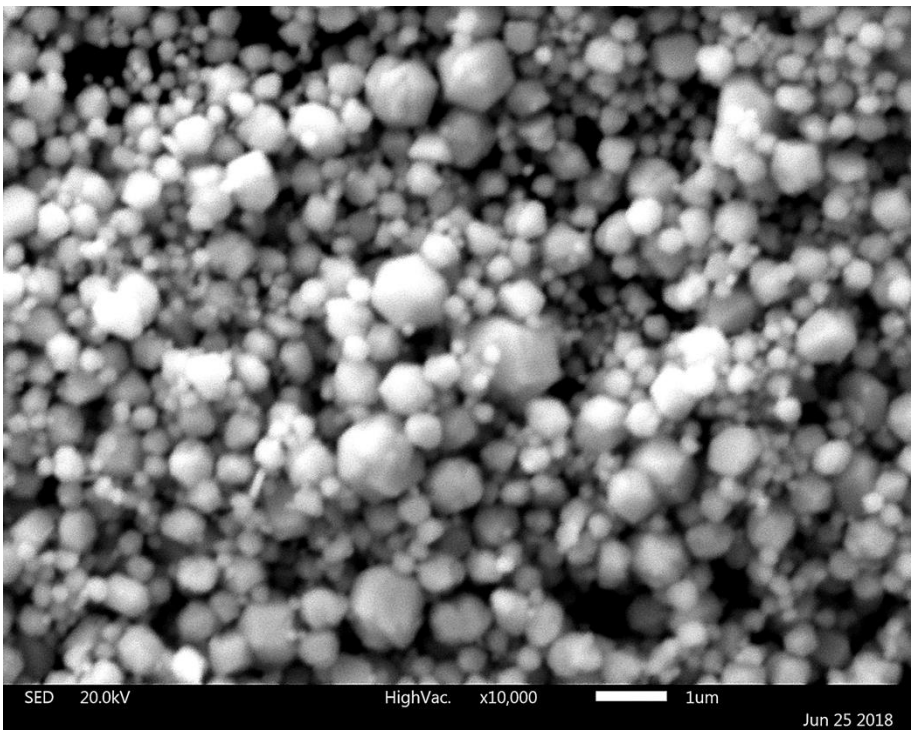

Figure 1. Silver powder after reduction of Ag^+(45 g/L) with ascorbic acid (30 g/L); 10 g/L PVP

The benefit of the method is that it is simple, inexpensive, and good enough for fine powder with particles with a size of 1-2 μm. As can be seen in figure 1, silver powder has a wide distribution of particle size, which is the main disadvantage of the procedure. Particle size is mainly from 300 nm up to 3 μm, with the majority in the interval from 500 to 2000 nm. Although smaller particles were nearly spherical, the larger were mainly polyhedric, which was not preferable but tolerably since the large aggregates in great numbers have the hexagonal intersection with good packaging characteristics. The picture suggests two parallel mechanisms, agglomeration for smaller and near-spherical particles and aggregation for the larger.

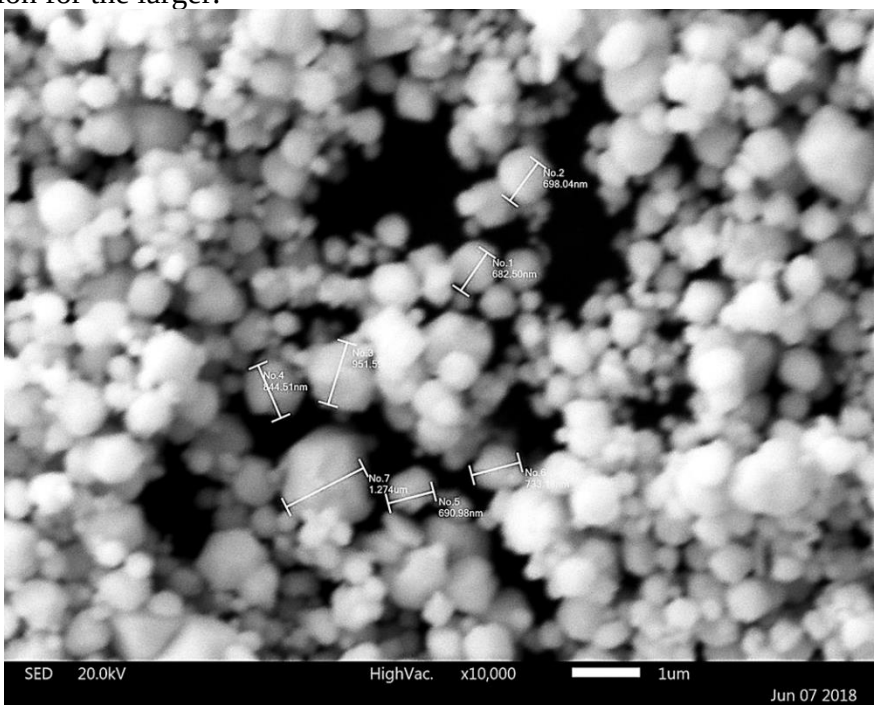

Figure 2. Silver powder after reduction of Ag^+(30 g/L) with ascorbic acid (20 g/L); 10 g/L PVP

Optimization of the process could be performed differently. In this study, priority was to keep the yield of the process near 100% and to use concentrations as high as possible to achieve lower production costs. With this strategy, very good results are obtained by lowering the concentration of silver on 30 g/L and ascorbic acid in the same percentage (down to 20 g/L). The concentration of PVP also needs to be as low as possible, and it was kept at 10 g/L. The value of pH was raised and kept between 7 and 8. Powder obtained with these parameters is presented in figure 2.

The narrower size distribution of the particles is obvious, as shown in figure 2. Particles are about 1000 nm on average. Small rulers in the figure for particulate grains illustrate that fact. Size for the measured particles ranged from 682 to 1274 nm. Agglomeration is obvious, but agglomeration occurs in two stages, from nanoparticles (about 100 nm), also visible in the figure, to particles with size about 250-300 nm witch made final particles. A small sample (not statistically important) that measured by SEM has an average size of approximately 840 nm. Particles are more spherical than in the previous experiment.

Further improvement of the technology was the change of the dispersant. The use of gelatin instead of PVP has given even better results and lower costs. The same concentrations of reaction reagents as with PVP were used for the optimal results of the experiments. The concentration of gelatin was much lower than PVP concentration and was 1:40 in mass ratio against Ag (0.75 g/L). The resulting powder with this modification is shown in figure 3.

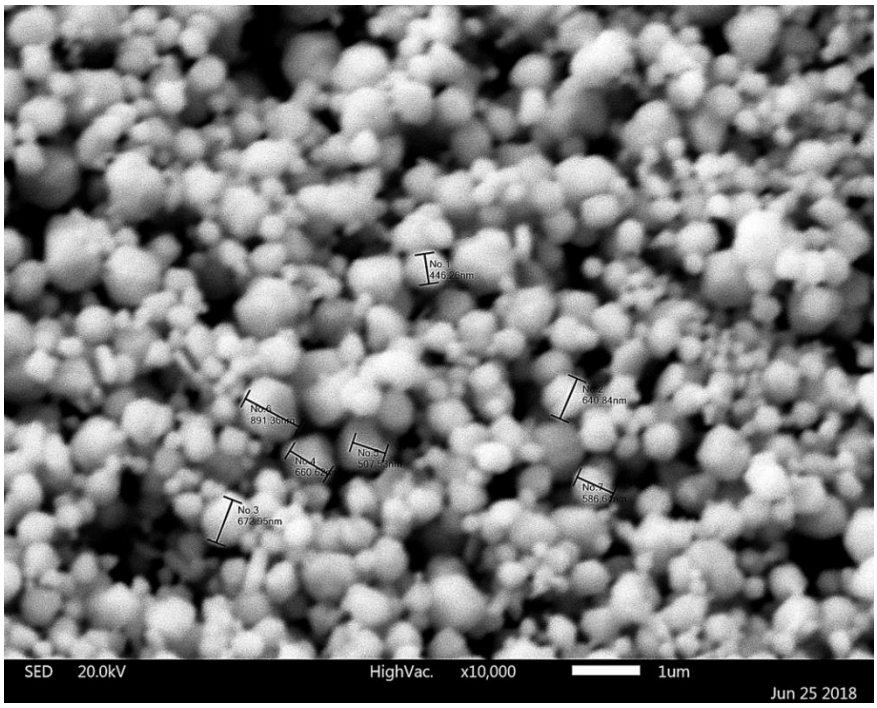

Figure 3. Silver powder after reduction of Ag^{+}(30 g/L) with ascorbic acid (20 g/L); 0.75 g/L gelatin

The improvement over the use of PVP is in the more spherical particles than both experiments with PVP as a dispersant (protecting agent), smaller particles, and lower costs (not just that gelatin is less expensive than PVP, but the lower concentration is needed). From figure 3 it can be seen that most of the particles are from 200 to 1000 nm. Characteristics particles were measured and ranged from 446 to 891 nm, with an average size of nearly 630 nm. This powder was measured by laser diffraction, and the results are shown in figure 4.

As can be seen from figure 4, laser diffraction (LD) has given a higher average value for the particle size than SEM which is known from the literature. Nevertheless, the agreement between these two methods is good enough. Figure 4 also illustrates quite a narrow size distribution, LD gives values from 0.5 to 2 μm, and the average value of about 1 μm. The cumulative curve also shows that about 80% of the particles are smaller than 1.5 μm.

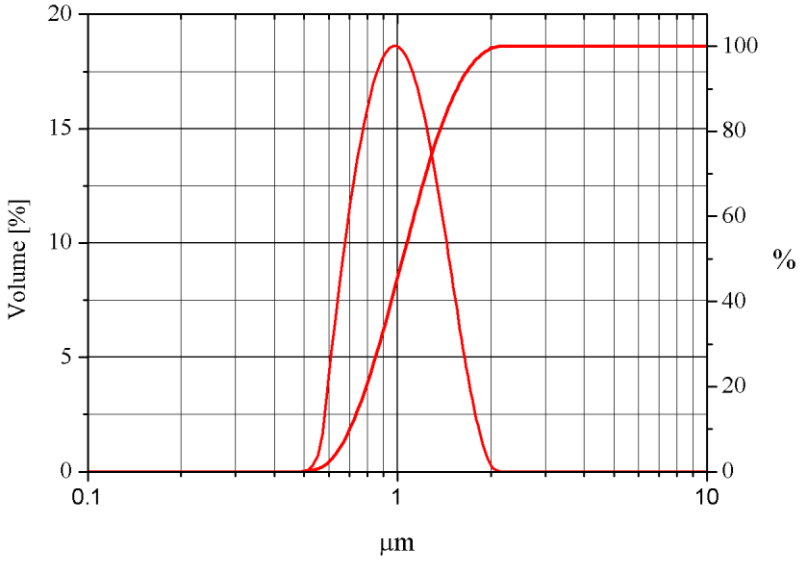

Figure 4. Granulometric composition of the powder obtained by use of gelatin, 1:40 vs silver

4 Conclusions

The study has shown that even high concentrations of reagents (silver ions and ascorbic acid) and low concentration of PVP can produce a silver powder with an average size between 1 and 2 μm. The disadvantage of that reaction parameter is the very wide size distribution of the particles.

Optimization of parameters with the same reagents gives better results, with the average size of nearly 1 μm and narrower size distribution of the particles. Further improvement was achieved by the use of gelatin instead of PVP polymer. Smaller and more spherical particles with a further decrease of the size distribution are obtained. This silver powder can be used for the thick film technology that would be applied in the solar energy industry.

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