

The X-ray activated reduction of silver (I) solutions as a method for nanoparticles manufacturing

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Materials

ABSTRACT

Purpose: The aim of this work was to determine an effect of X-ray irradiation on activation of silver reduction from water solutions of its salts, resulting in fabrication of nanocrystalline product.

Design/methodology/approach: The process and products of the reduction of silver nitrate water solutions, containing the additions of other compounds or not, including particle growth inhibitors, irradiated with X-rays of different energy or with a laser beam, were investigated.

Findings: It was found that irradiation had significant effect on the initiation of the reduction process and on its rate and proceeding. The radiation dose is not of great importance provided that some its threshold value is exceeded. It was also found that polyvinyl pyrrolidone (PVP), used as growth inhibitor of silver crystallites, exhibits a reducing effect in the studied processes.

Research limitations/implications: It is recommended to perform further research aimed at increasing mass yield of irradiation-activated reduction process and at selecting efficient method for deposit separation from the solution at the maintained high refinement of silver particles.

Practical implications: The results from this study extend the scope of available methods for preparation of silver nanoparticles by a new one, which is based on process activation by irradiation of the substrates by X-rays.

Originality/value: The new method for silver nanoparticles fabrication has been successfully tested and its usefulness has been proved. Conditions for conducting the process of silver (I) ions reduction by this method have been proposed.

Keywords: Nanomaterials; Silver nanoparticles; Hydrometallurgy; Reduction

1. Introduction

Studies have been conducted for many years in many research centres on nanocrystalline silver. They are concentrated not only on searching for new applications but also on new methods for its fabrication. Considering the recent state-of-art, classical techniques such as chemical, thermo-chemical or hydro-metallurgical technologies are not competitive to the physical

methods, such as evaporation and rapid condensation [1]. This work was aimed at extending the scope of classical hydrometallurgical method based on precipitation of metallic silver from water solutions of its salts under the influence of radiation. This method has been used by Singh et al [2], who activated the solutions by means of laser radiation. The irradiation methods with the use of laser or electron beam in order to modify the properties of materials were also applied by Dobrzański et al [3]

and Żenkiewicz et al [4]. Moreover, the attempts were made to find surface-active substances [5-10], which inhibit growth of particles after adding them to the reduced solutions. It was reported, that polyvinyl pyrrolidone (PVP) can be successfully used as such a inhibitor. In this work, X-ray radiation was used as a factor initiating the reaction of silver precipitation from the solutions of its salts, and the obtained results were compared with those from previous studies conducted with the use of other methods [2,5-10].

2. Material for the investigation

In the tests of silver powder fabrication, water solutions of AgNO_3 with or without an addition of NH_4OH were used. In some cases sodium hydroxide was added in order to ensure suitable pH of this solution. As a reducer, solutions of the substances exhibiting very weak reducing properties were used, the presence of which in water solution of an examined salt should not result in a spontaneous initiation of silver reduction. The reducing agents were glucose, invert sugar, citric acid, ascorbic acid, sodium-potassium tartrate, trisodium citrate and hydrazine. The PVP was used as a surface-active agent inhibiting crystals growth and formation of the agglomerates.

3. Solution activation methods

3.1. Activation by the "soft" X-ray radiation

For this purpose non-filtered ("white") radiation of a cobalt lamp from the URD 6 X-ray diffractometer has been applied. Operating parameters of the X-ray lamp were 30 kV/30 mA. The activated solution was placed in a thin-walled polyethylene vessel, and it was positioned along the path of the X-ray beam. An area of about 1 cm x 1 cm was irradiated through the walls of this vessel. The solution was mechanically stirred and the exposure times were 1 and 4 hours.

3.2. Activation by "hard" X-ray radiation

Non-filtered radiation of a tungsten lamp from the TUR D701 X-ray apparatus was used. Operating parameters of the lamp were 110 kV/125 mA. The irradiation method was the same as that described in point 3.1. The exposure times were 2, 6 and 18 seconds. The solutions were not stirred.

3.3. Activation by a laser beam

The Trumpf Lasercell TLC 1005 equipped with CO_2 laser was used for irradiating the solutions. The defocused radiation beam with a wavelength of 10.6 μm and power of 350 W formed a circle about 3 mm in diameter on a top surface of the liquid. Exposure time was 6 minutes. The irradiated solution was stirred by means of magnetic stirrer and cooled in a water bath.

3.4. Thermal activation and comparative tests

The vessels with examined solutions were placed for 1 hour in a water bath at the temperature of about 60 $^{\circ}\text{C}$. The solutions were stirred with magnetic stirrer. The reference solutions of the same composition as the irradiated ones, but not subjected to activation, were analysed as well. The reference material was also a deposit obtained by the chemical method described by Yiwei Tan [6], which is based on application of the AgNO_3 solution with an addition of PVP as grain growth inhibitor, and with formaldehyde and triphenylamine as reducing agents.

4. Methods of analysis

4.1. X-ray structural analysis

Phase analysis of the obtained precipitates and measurements of their crystallite size were made from the diffraction patterns obtained using XRD7 X-ray diffractometer with $\text{Co K}\alpha$ radiation. The phase identification was carried out using the data [11,12]. Crystallite size was determined by the Scherrer method [13]. The analysis of micro-stresses [14] was made, which confirmed that they had no significant effect on the results.

4.2. Sedimentation analysis

Particle size of the formed precipitates (single crystallites or polycrystalline agglomerates) was determined by sedimentation method using Micromeritics SediGraph 5100 instrument. Water suspensions of the precipitated products, homogenized by means of ultrasonic stirrer, were analysed.

4.3. Reaction efficiency determination

The filtered precipitates were dried in a vacuum desiccator into a solid mass and then weighed on analytical balance together with a filter with an accuracy up to 0.0001 g. Relative yield of the reaction was calculated from the masses and quantitative phase compositions of the precipitates.

5. Results and discussion

The results from preliminary tests were used to eliminate these reducing solutions, which exhibited too strong reducing properties. In the majority of tested solutions the reactions proceeded spontaneously and usually rapidly, leading without irradiation to the growth of relatively coarse-grained precipitates, which contained also considerable amounts of other phases, mainly Ag_2O . Only the solutions containing relatively weak reducers (including glucose in a form of water solution with the concentration of 0.03% and citric acid water solutions with the concentrations of 5% and 0.025%) were subjected to irradiation. They were added to the solution of silver (I) in a 1:20 proportion.

Table 1.
Results of silver nanoparticles fabrication from PVP-containing solutions subjected to different activation methods

Method	Activ. time	Results	"PVP"	"PVP+dca"	"PVP+ca"
"Soft" X-ray irradiation	1h / 4 h	Deposit	Ag / Ag+o	Ag / Ag+o	cit +Ag / cit +Ag +o
		a_{Ag} , [%]	100 / 87	100 / 89	9 / 10
		Φ_{Ag} , [nm]	17 / 11	16 / 14	16 / 16
		Y_{Ag} , [%]	17.2 / 18.6	26.3 / 29.8	22.1 / 22.2
"Hard" X-ray irradiation	2s / 6s / 18s	Deposit	Ag / Ag / Ag	Ag / Ag / Ag	cit +Ag / cit +Ag / cit +Ag +o
		a_{Ag} , [%]	100 / 100 / 100	100 / 100 / 100	11 / 11 / 12
		Φ_{Ag} , [nm]	14 / 16 / 13	15 / 14 / 15	15 / 12 / 13
		Y_{Ag} , [%]	23.6 / 25.3 / 25.2	30.4 / 33.1 / 34.6	19.1 / 19.9 / 22.6
Laser beam irradiation	6min.	Deposit	Ag	Ag	cit +Ag +o
		a_{Ag} , [%]	100	100	34
		Φ_{Ag} , [nm]	12	16	12
		Y_{Ag} , [%]	11.5	25.8	18.0
Temp. 60 °C (water bath)	1h	Deposit	Ag	Ag	cit +Ag
		a_{Ag} , [%]	84	86	7
		Φ_{Ag} , [nm]	19	24	23
		Y_{Ag} , [%]	18.9	24.9	21.7
No activation (reference sample), 24 h after preparing the solution		Deposit	Ag	Ag	cit +Ag
		a_{Ag} , [%]	100	100	48
		Φ_{Ag} , [nm]	15	13	12
		Y_{Ag} , [%]	10.0	10.8	9.7
Chemical method acc. to the procedure from [6]		Deposit		Ag	
		a_{Ag} , [%]		100	
		Φ_{Ag} , [nm]		31	
		Y_{Ag} , [%]		100 def.	

Legend:

- PVP – symbol of a solution containing 1.7 g AgNO₃ and 6.8 g PVP in 100 cm³ of distilled water,
PVP+dca – like "PVP" + 5 cm³ of a citric acid solution (0.025%),
PVP+ca – like "PVP" + 5 cm³ of a citric acid solution (5%),
 a_{Ag} – mass fraction of metallic silver in the precipitate,
o, cit – symbols of detected alien crystalline phases of the silver oxide Ag₂O (o) and silver citrate Ag₃C₆H₅O₈ (cit),
 Φ_{Ag} – diameter of metallic silver crystallites,
 Y_{Ag} – relative yield of the reaction of metallic silver fabrication, in comparison with that for the chemical method.

The next step was aimed at eliminating glucose-containing ammonia solutions. The reactions taking place in these solutions resulted sometimes in the formation of precipitates with unstable composition. These precipitates contained considerable amounts of silver nitride Ag₃N, which formed in some ammonia solutions of the silver salts and exhibited explosive properties in a dry state [15]. The results from analysis of the deposits obtained for three selected types of solutions are presented in Table 1.

As a result of analysis, the solution containing citric acid of a greater concentration has been eliminated since a great amount of silver citrate was formed in this case. The presence of small amounts of a citric acid, up to about 0.001%, resulted in the formation of greater amounts of precipitated metallic silver.

The differences in activation efficiency depended on activation time only to a small extent. Long exposure times resulted in partial oxidation of silver into Ag₂O. The impact of activation itself was evident since the amounts of silver obtained from irradiation-activated samples were significantly greater than in a reference sample, but these amounts were similar to those obtained as a result of activation initiated by the temperature increase. However, they were much smaller than the precipitate amounts obtained using chemical method, although on the other

hand, the degree of crystallites refinement was greatest in case of using irradiation methods. It can be stated, therefore, that activating of the solutions by irradiation leads to the formation of large amount of crystallisation nuclei and considerably speeds up initiation of the process of metallic silver precipitation. This confirms validity of the Brummer finding, related to activation of the reduction process of silver solutions by means of irradiation with UV-light or a laser beam [9], which occurs also in the case of activation with X-ray radiation.

The agglomeration process of silver nano-crystallites does not proceed at all or to a small extent. The sedimentation analysis showed that about 92 – 98% of a mass of the precipitates were particles with a diameter smaller than lower limit of measurability of the instruments used, i.e. 180 nm. Extrapolation of the experimental data to the values below 100 nm indicates that about 80 – 95% of a mass of analysed precipitates were nanoparticles.

A significant problem appeared to be the separation of such fine precipitates from the solution. The methods proposed in the literature [5-10], based on centrifuging of the reduction products in ultracentrifuge, lead to embedding of the finest precipitate fractions into the walls of centrifuge vessel, which in turn makes full separation of the precipitate from the substrate impossible.

There were also great problems with decantation of the obtained precipitate from the solution. Moreover, filtering resulted in a loss of a part of the precipitate, which penetrated through filter pores, and the losses were the greater the smaller were diameters of filtered precipitates. These are most probable reasons why the efficiency of the applied methods was much smaller in comparison with the chemical method applied in work [6], which is indicated by the data given in Table 1 and in Fig. 1. Mass of nanocrystalline silver fabricated by the chemical method was considerably higher than that obtained using irradiation methods. However, crystallite diameters from the chemical method are much greater, which enables full or almost full separation of the precipitates with this grain size, which is troublesome in case of irradiation-based method applied under the conditions described in this work.

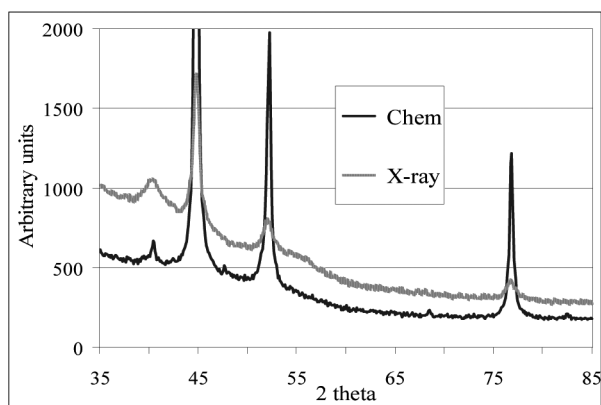


Fig. 1. The X-ray diffraction patterns for silver precipitated from the "PVP" solution after irradiation with a beam of "hard" X-ray radiation for 2 seconds (grey line) and obtained by the chemical method (black line). The difference in intensity and width of the diffraction lines for these precipitates is seen.

6. Conclusions

1. The irradiation with X-rays, and to a smaller extent, energy of this radiation, have significant effect on the rate and intensity of the initiation of silver reduction from its nitrate solutions and precipitation of metallic silver. This effect is observed mainly at the beginning of the process, after its initiation this effect decreases. The irradiation dose is not of great importance provided that some minimum value is exceeded.
2. Under the assumed conditions of the reaction, PVP acts not only as inhibitor of silver crystallite growth but also as very mild reducer, which enables fabrication of suitably fine precipitates.
3. The optimal procedure for fabrication of silver nanoparticles by the irradiation method is based on using high-energy X-ray beam to irradiate a solution containing only silver nitrate and PVP, without additional reducers or only with an addition of citric acid with the concentration of 0.001%. This procedure makes it possible to obtain silver crystallites with the diameters up to 20 nm.
4. The problem to be solved is the choice of an efficient method for the extraction of nanocrystalline particles from post-reaction solution.

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