

Photo-induced chemical reduction of silver bromide to silver nanoparticles

Research Article

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Abstract: This paper discusses the experimental results of the production of nanocolloidal silver using photoreduction method. Ultrafine crystalline gelatine-stabilised aqueous suspensions of silver bromide were used as a substrate for the synthesis of silver nanoparticles ($Ag\ NPs$). The influences of the reductant to substrate molar ratio, the medium's pH, the type of the source of actinic radiation and the time of exposure to the efficient production of the $Ag\ NPs$ were studied. A typical reaction was suggested, which involves the photo-induced reduction of silver bromide nanocrystals in the presence of ascorbic acid under specified physicochemical conditions. The properties of resultant silver particles were examined using UV-Vis spectroscopy and Dynamic Light Scattering (DLS). In addition, Transmission Electron Microscopy (TEM) was used for imaging the silver nanoparticle suspensions.

Keywords: Silver • Silver nanoparticles • Silver bromide • Ascorbic acid • Photoreduction

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1. Introduction

Interest in nanostructural silver comes from its bactericidal, antiviral, fungicidal properties and specific physical and optical features [1-8]. Properties shown by silver on a nanometer scale urge the exploration of further methods of producing, stabilising, examining their properties and developing new technological applications for the materials useable in designing plasmonic solar cells, cathodoluminescence plasmon microscopy, optical metamaterials etc. [9-11].

A number of methods have already been developed to produce materials containing nanostructural silver. The most popular ones are photochemical reduction, chemical reduction, radiolysis, biosynthesis of silver nanoparticles, laser ablation, sonochemical method and microwave radiation [12-21]. The $Ag\ NPs$ are most often synthesised by chemical reduction [22-24]. How fast the metal particles will grow depends on the reductant's structure and its redox potential and the properties of the medium in which a reaction occurs. Silver nitrate is generally used as a source of silver ions during this process, whereas silver nanoparticles are synthesised in the form of a colloid, most often in the presence of a polymer stabiliser. Technology of producing

nanostructural silver by using, *inter alia*, methods of the photochemical decomposition of silver salts [25,26], is now a very attractive research field as well. For photochemical decomposition of silver salts, very small colloidal particles can be achieved, and the reduction of metal ions can be controlled through the control of the exposure time. This technology involves, above all, the photolysis of silver nitrate or silver perchlorate. However, nanoparticles populations obtained using the methods indicated above show a distribution of sizes and habits, and therefore research into efficient production of possibly monodisperse suspensions of nanocolloidal silver is continued [27-30].

Studies using $AgBr$ as the precursor for $Ag\ NPs$ were described in [31-33]. S. Liu and co-workers showed preparation of long silver nanowires from $AgBr$ nanocrystals (35 nm) and tabular silver bromide crystals [31,32]. These authors used the photographic developers as the reducing agent. R. Lahtinen *et al.* reported a two- phase synthesis of $Ag\ NPs$. That method involved the preparation of a stable negatively charged $AgBr$ hydrosols, transferring the hydrosols to an organic phase by means of $TOABr$, and borohydride reduction in the presence of a thiolate ligand [33].

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This study uses the photoreduction method, which merges the photolysis and the chemical reduction of photosensitive silver salts. Silver bromide suspensions with nanometer crystal sizes served as a substrate for producing nanostructural silver. As compared to generally used silver nitrate and silver perchlorate, an advantage of using a hardly soluble silver salt such as AgBr is that you can maintain a fixed yet appropriately low concentration of silver ions in the solution. Such a concentration results from the thermodynamic equilibrium defined by the solubility product of this salt, which enables silver ions be released slowly to the medium, making it quite easy to control the crystallisation of nanostructural silver.

L-ascorbic acid was used as a reducing agent. Silver bromide is reduced with ascorbic acid in a molar ratio of 2:1, with a surplus of silver ions, as shown in the Fig. 1. Chemical mechanism of this process can be found in the literature [38].

The Ag NPs were prepared in water solution of photographic gelatine – a natural protective colloid, impending nanostructural silver formation. The degree of crystals formation retardance, described by PR value (*Physical Retardance*), can be determined by using *PAGI METHOD* standards [34]. Gelatine with PR value 40 was used as Ag NPs stabilizer.

Research into the production of nanocolloidal silver using photo-induced chemical reduction of silver bromide crystals was carried out in wide range of molar ratio AgBr to ascorbic acid (0.1-2.0), pH (4.0-13.0) and actinic radiation (emitting from halogen, xenon and mercury lamps). The results presented in the paper are the most satisfactory and the criteria were the time (which do not exceed 90 min) and the size (under 40 nm of diameter) of synthesized Ag NPs. A series of experiments were conducted to identify the physicochemical conditions for the synthesis of Ag NPs, which were recognised as standard and assumed to be a typical reaction. We employ this reaction successfully in studying the efficiency of the photoreductive decomposition of photosensitive silver salts doped with metal ions or sensitised spectrally.

We also examined the influence of light and sodium sulphite on the efficiency reduction of AgBr. Research into preparation of Ag NPs using photolysis of AgBr were conducted and characteristic absorption band maximum for resultant Ag NPs in the range of 390 – 430 nm was not observed using this method. Sodium sulphite is a weak

reducing agent of AgBr in the investigated conditions. Ag NPs with characteristic plasmon absorption maximum were not obtained in the presence of sodium sulphite.

2. Experimental procedure

The reactions were staged in a special darkroom with dark red protective lighting at 22°C. Temperature was monitored during the synthesis and significant fluctuations of temperature during irradiation were not observed. Suspensions of silver bromide crystals (average diameter 60 nm) were used as a substrate for the synthesis of nanocolloidal silver. Silver bromide crystals suspensions were obtained using new, modified method of preparation Lippmann's suspensions which is described by A. Dyonizy et al. [35].

Put into a reaction vessel in the form of a 100 mL large quartz cuvette was 1 mL of 0.333 M silver bromide crystal suspension, which was then diluted with water down to 70 mL. Subsequently, the substances were added to ensure the appropriate pH of the medium: sodium carbonate (pH=10.0), trisodium phosphate (pH=11.0-12.6), sodium hydroxide (pH=13.0) and ascorbic acid as reducing agents, and sodium sulphite was added to prevent the oxidisation of ascorbic acid to dehydroascorbic acid. The whole vessel was filled up with redistilled water up to 100 mL. The total concentration of the AgBr crystal suspension in the solution was 3.3×10^{-4} M, and that of the gelatine was 0.5 g dm⁻³. The experiments were conducted with or without the exposition to actinic radiation of the reaction mixture, which was being stirred vigorously throughout the whole process of synthesis. The photoreduction of silver bromide crystals was initiated with a two-minute exposition or supported with exposition during the whole reaction using a halogen lamp (1000 W POLAM LH21) or a high-pressure mercury lamp (200 W Narva HBO 200), respectively. An Elfo Maxflash 500 xenon flash lamp was also used to initiate the photoreduction process. The distance of the cuvette from the source of electromagnetic radiation was 20 cm. UV-Vis spectra were generated using an OceanOptics USB-4000 optical fibre spectrophotometer. Process of preparation of Ag NPs from silver bromide crystals suspensions was conducted to its final stage that means authors did not observe any changes in UV-Vis spectra in duration of the synthesis. Transmission Electron Microscopy

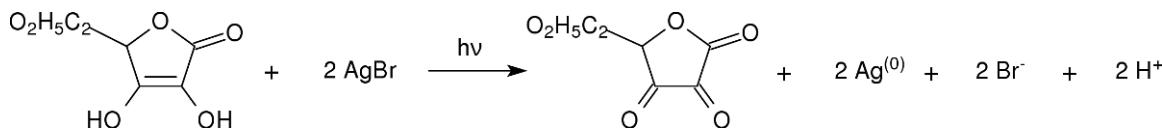


Figure 1. Scheme of reduction of silver bromide with ascorbic acid.

images were taken using PHILIPS EM 301 microscope, with an accelerating voltage of 80 kV. Microscope specimens were prepared by depositing the colloid onto formvar 15/95E polymer-coated copper grids. Dynamic Light Scattering measurements were carried out using Nicomp 380 ZLS equipment, with a laser light wavelength of 573 nm and a temperature of 22°C. The concentration of the testes solutions was 3.3×10^{-5} M. The study used analytical purity reagents manufactured by POCH S.A. Poland.

3. Results and discussion

3.1 Influence of the AgBr to ascorbic acid molar ratio

The experiments were conducted as described above. The sample was exposed to a high-pressure mercury lamp for the entire duration of the synthesis, with an estimated pH of 10.0 and the total reaction time not exceeding 90 min. The medium contained silver bromide in the following molar ratios to ascorbic acid: 1:1.5, 1:3.0, 1:4.5 and 1:9.0.

Fig. 2 gives UV-Vis absorption spectra of the products obtained in molar ratios described above. The Ag NPs synthesized in molar ratio AgBr to reductant of 1:1.5, 1:3.0, 1:4.5 and 1: 9.0 present absorption peaks at 429, 428, 419 and 389 nm, corresponding to full width at the half-maximum (*fhwm*) of 145, 120, 110 and 55 nm, respectively. The absorption peaks shifted to shorter wavelength and became narrower with the elevated molar ratio, possibly due to the decrease in size [36,37]. The plasmon effect, which is typical of spherically shaped Ag NPs, occurs in the range from 390 to 425 nm, corresponding to particle size from 4 to 50 nm [37]. Ag NPs prepared in molar ratio 1:4.5 and 1:9.0 presented an additional absorption in the long-wave part of the spectrum. This absorption may be a sign of larger silver particles also formed under such conditions, with a shape different from spherical and varying axial ratios. It was recognised that the time needed to convert the substrate shortens as the reductant concentration is increasing in the reducing mixture e.g. 5 min for molar ratio of 1:9.0, 30 min for 1:4.5 and 60 min for 1:3.0, 90 min for 1:1.5.

Based on the experiments, an ascorbic acid to silver bromide molar ratio of 3:1 was selected for further research into the photoreductive decomposition of silver bromide. Duration of reaction, the best result of the experiments and the conviction that in such conditions silver bromide is almost completely converted into silver nanoparticles (Fig. 3) were the main reasons why excess reductant was used.

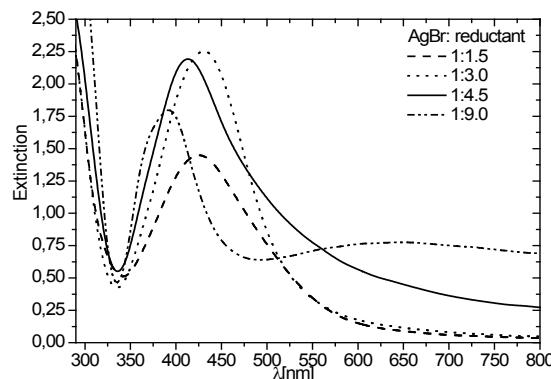


Figure 2. UV-Vis spectra of silver nanoparticles recorded during the photoreduction of AgBr crystals in the presence of ascorbic acid. The individual curves represent the various molar ratios of AgBr to ascorbic acid: 1:1.5, 1:3.0, 1:4.5 and 1:9.0.

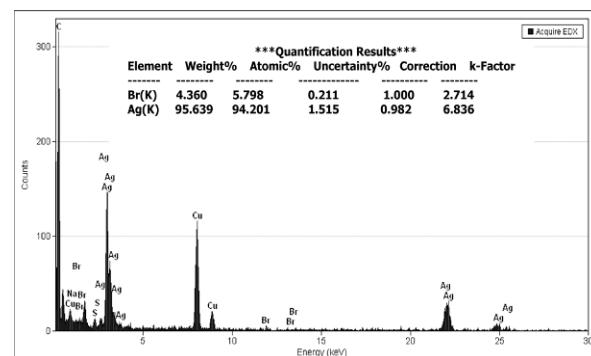


Figure 3. EDX spectra of the Ag NPs, Cu and C peaks appear due to scattering caused by the carbon film and copper of the TEM grid. EDX spectra present results of reaction in molar ratio AgBr to ascorbic acid 1:3.0 after 60 min.

3.2 pH Influence

Another step was to determine how efficiently silver nanoparticles are generated through the photoreductive decomposition of silver bromide, depending on the acid-base equilibrium of the reaction medium. Various substances were added to the reaction medium to ensure an appropriate predefined pH. The experiments were conducted in the presence of actinic radiation from a high-pressure mercury lamp, for an ascorbic acid reactants to silver bromide molar ratio of 3:1. Experiments to study the efficiency of the photoreductive decomposition of silver bromide crystals which depends on the medium in which a reaction occurs were performed for a pH range of 10.0 to 13.0. An alkaline medium was selected because it is known that ascorbic acid is slowly oxidized in an acidic or neutral environment but it reacts rapidly with silver halide in alkaline solutions [38]. Accordingly, nanostructural silver was obtained for a pH of below or equal to 7.0 only after a very long time of synthesis, i.e., approximately twelve hours.

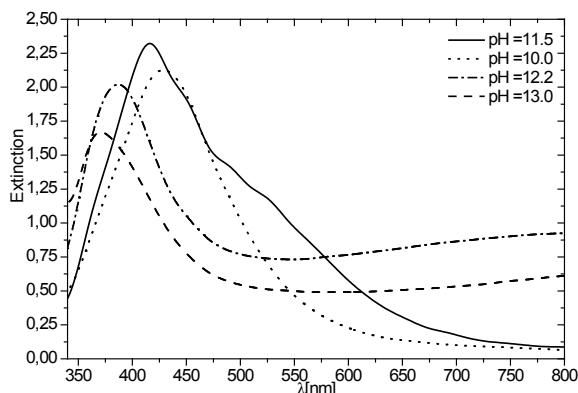


Figure 4. UV-Vis spectra recorded during the photoreduction of AgBr crystals in the presence of ascorbic acid, with an AgBr to ascorbic acid molar ratio of 1:3.0, various pHs and with exposition to light.

Fig. 4 presents UV-Vis spectra of the products obtained after reactions with exposure to light. The ultra-fine crystalline suspensions photo-reduced at pH 10.0, 11.5, 12.2 and 13.0 presented absorption peaks at 430, 409, 389, 376 nm, corresponding to fwhm of 129, 112, 79 and 73 nm, respectively. When pH value increases the absorption peaks shifted to shorter wavelength with decreasing fwhm, possibly due to decreasing particle size. Based on the test results presented in Fig. 4 it was found that during exposure to a high-pressure mercury lamp in a strong basic medium with pH=12.2-13.0 silver bromide reduced to metallic silver instantly (1 min) but showing the anisotropic character of the particles, relating to absorption in the long-wave part of the spectra. Under the same conditions with pH=13.0, when the process was not initiated by actinic radiation (Fig. 5), the reaction proceeded much slower (90 min), producing the expected results in the form of colloidal silver suspension possibly with a noticeable size and shape dispersion. This is due to the additional absorption in the long-wave part of UV-Vis spectra, as evidenced by the great value fwhm of 165 nm. Changes in the UV-Vis spectra are negligible while the process of silver bromide crystals being reduced to nanostructural silver is practically non-existent when pH is equal to 10.0 and 11.5, when this reaction is not initiated by actinic radiation (Fig. 5). The probable reason for the lack of reduction reaction in the absence of light in the pH in range from 10 to 11.5 in the presence of gelatine is that the value of the oxidation-reduction potential barrier is too high for ascorbic acid to reduce the crystals of silver bromide to silver. It is necessary to initiate this reaction e.g. by applied actinic radiation allowing the formation of doped centers in the form of clusters of silver on the surface of silver bromide crystals, which are converted into silver nanoparticles in the presence of ascorbic acid.

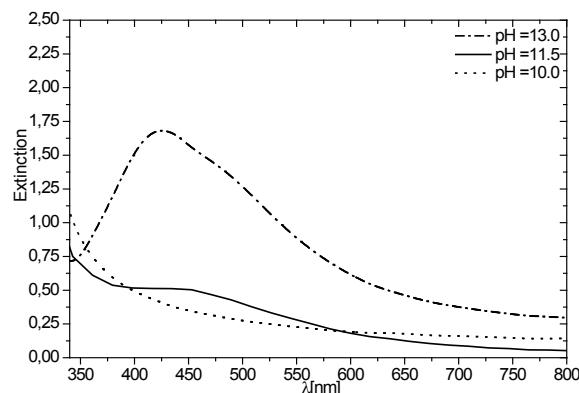


Figure 5. UV-Vis spectra recorded during the reduction of AgBr crystals in the presence of ascorbic acid, with an AgBr to ascorbic acid molar ratio of 1:3.0, various pHs and without exposition to light.

A simple correlation was noticed when silver particles were obtained through exposure to actinic radiation, and namely that the higher pH the medium had the shorter the reaction time was. For instance, the time needed for AgBr to be completely converted into metallic silver when pH=10.0 was 60 min, whereas for pH=13.0 it was substantially reduced to 1 min.

Analysis of the results obtained made it clear that the reaction is most advantageous for pH=10.0 when exposure to actinic radiation from the high-pressure mercury lamp is used. The reaction conditions described above were selected for further research into the photoreductive decomposition of silver bromide in an alkaline medium.

3.3 Influence of actinic radiation

The effect of reaction mixture exposure time on Ag NPs production efficiency using various sources of electromagnetic radiation from high-pressure mercury-vapour, xenon flash or halogen lamps was investigated. The process was conducted according to the standard procedure described before, under the condition of pH=10.0, with the presence of ascorbic acid and sodium sulphite. It should be stressed that instead of the effect of the intensity of actinic radiation it was the efficacy in increasing the efficient decomposition of silver bromide to nanostructural silver that was examined. All the above-mentioned radiation sources have different spectra and emit radiation with different ranges. The xenon flash lamp has a specific spectrum in the light range and shows a high intensity of infrared radiation. The mercury lamp has a band spectrum and emits relatively more UV radiation. The halogen lamp, however, has a continuous spectrum within an interesting spectral range.

As the literature suggests, electromagnetic radiation (photochemical method) or chemical reductant (chemical reduction) can be used to obtain various silver nanoclusters on silver bromide crystals [39]. Namely, one Ag nanocluster is formed on one silver bromide grain (e.g. with a diameter of approx. 5 nm) due to the photoreductive decomposition of AgBr, and after chemical reduction it is 200 silver nanoclusters on the same AgBr grain. Thus, the resultant nanoclusters show similar plasmon absorptions that are typical of nanostructural silver. The scheme of how Ag nanoclusters are formed is shown by Tani [40]. The reduction of silver bromide produced Ag₂ dimers, which are stabilised where surface defects are found, serving as reduction and coagulation centres for the forming of silver nanoclusters. The process of silver clusters being formed due to the chemical AgBr reduction is quite different from that of silver clusters being formed in the photochemical method [40]. The latter is based on the forming of silver clusters as a result of one atom after another being attached to the centre, where a photoelectron and an interstitial silver atom are captured. These two processes take place in the experiments described. First, the forming of nanostructural silver is initiated photochemically, and then silver nanoparticles grow according to the chemical reduction mechanism of silver bromide crystals.

Based on the spectroscopic measurements taken after 30 min of the synthesis, it was demonstrated that the photoreduction of silver bromide to metallic silver is most efficient for exposure to radiation emitting from the halogen lamp (Fig. 6). This is probably caused by the fact that the radiation emitted by the halogen lamp is the strongest. Photoreduction using this type of radiation is the most efficient, although practically this source generates low radiations levels within the characteristic absorption range of silver bromide, which spans from ultraviolet to approximately 480 nm. UV-Vis spectra recorded after the completion of each synthesis, carried out using various sources of actinic radiation, did not show any significant differences. No change in the location of the absorption maximum was observed, which can be identified with the production of colloidal suspensions of silver particles featuring similar sizes and shapes. The photoreduction time for which radiation from the xenon and halogen lamps was applied was approximately 60 min. For the mercury lamp, however, this time was extended to approximately 90 min, as the radiation generated by this lamp has a lesser effect on silver bromide. Although the high-pressure mercury lamp shows a relatively higher share of radiation within the range corresponding to the characteristic absorption of silver bromide, the photoreduction process was the

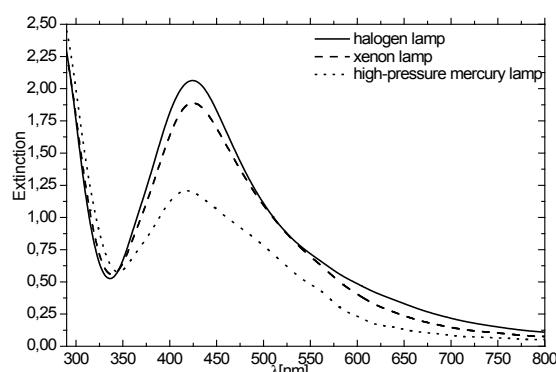


Figure 6. UV-Vis spectra recorded after 30 min of each AgBr photoreduction with ascorbic acid (molar ratio of AgBr to ascorbic acid 1:3.0, pH=10.0, in the presence of Na₂SO₃) using exposure to radiation with various spectral characteristics (halogen, xenon and high-pressure mercury lamp).

slowest because this lamp has a rather low power output. It turns out to be beneficial to initiate the AgBr photoreduction using continuous actinic radiation with high intensity when you want to enhance the efficiency of the reaction while substantially reduce its duration.

Experiments were also performed to examine how the efficiency of the photoreductive decomposition of silver bromide differs between the reduction with a two-minute initiation by electromagnetic radiation and that with the continuous exposure of the sample during the experiment. The experiments were carried out using radiation from the halogen lamp. It was concluded from these experiments that the same result is produced when the reaction mixture is exposed for two minutes, i.e., Ag NPs are obtained using silver bromide as a substrate as efficiently as when reactants are exposed for the whole duration of the reaction. In further tests, it was decided therefore to use a two-minute initiation of the photoreduction by radiation from the halogen lamp.

3.4 Characteristic reaction

Based on the experiments conducted, a characteristic reaction was suggested which involves the photoreduction of AgBr crystals in the presence of ascorbic acid. It uses ascorbic acid in a threefold molar excess compared with silver bromide, in the presence of sodium sulphite, with the reaction's pH of 10.0, a 60-minute reaction time and a two-minute initiation of the reduction process by exposure to radiation from the halogen lamp. Fig. 7 shows the UV-Vis spectra recorded during the reaction in question. The absorption grows as time passes, which attests to the growth in the population of silver particles while they are formed. It was noticed when analysing the spectral curves that with the passage of the reaction time the absorption maxima moved to each curve, from 395 nm after

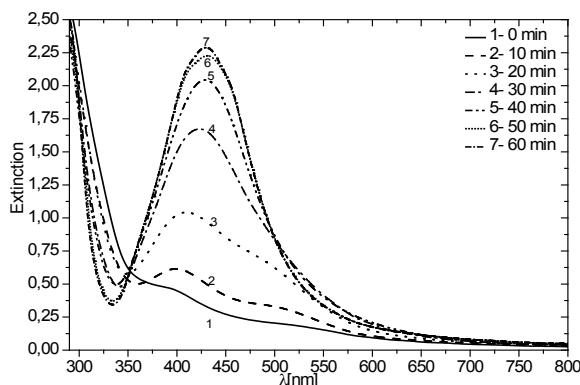


Figure 7. UV-Vis spectra of silver nanoparticles recorded during the photoreduction of AgBr nanoparticles in the presence of ascorbic acid – characteristic reaction.

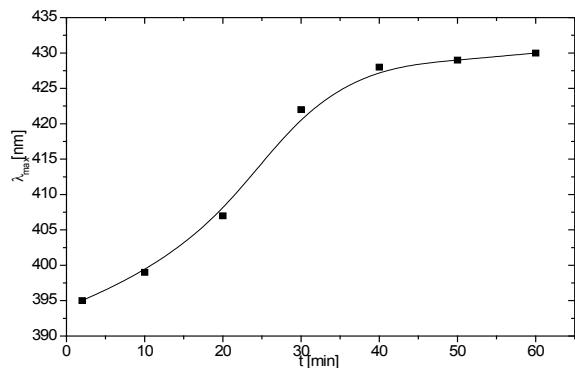


Figure 8. Position of an absorption band maximum of the Ag NPs obtained in different duration of the characteristic reaction

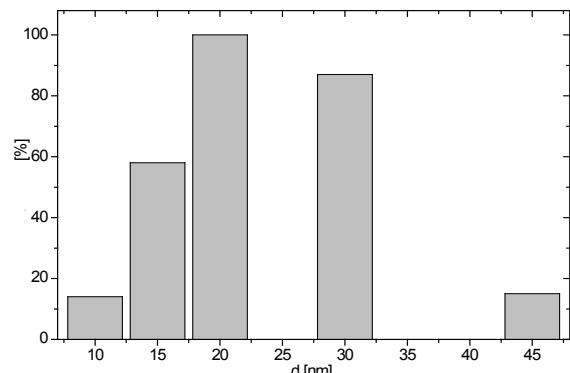


Figure 9. Volumetric size distribution of resultant silver nanoparticles obtained using the characteristic reaction.

two minutes of the process to 430 nm after 40–60 minutes of the reaction (Fig. 8). The direct result of the said process is a change in the colour of the reaction mixture, from violet-blue in the initial phase of the reaction to yellow-brown in its final stage.

Based on the Dynamic Light Scattering measurements, curves were plotted to show the relationships between the percentage volumes occupied by particles of a certain diameter in the tested

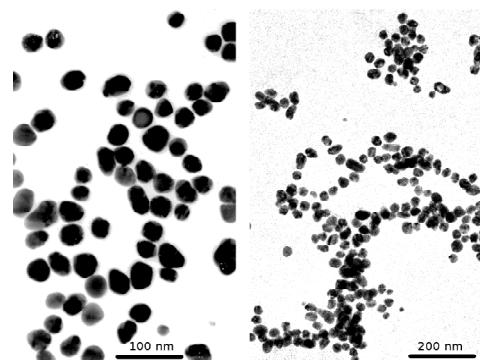


Figure 10. TEM images of resultant silver nanoparticles obtained using the characteristic reaction.

population. Fig. 9 shows the results measured for the resultant products of characteristic reaction concerned. This population predominantly contains silver particles with diameters ranging from 17 nm to 30 nm, with a clear distribution of sizes between 10 nm and 45 nm.

Analysis of the images obtained using the Transmission Electron Microscopy method (Fig. 10) and of the size distribution of silver nanoparticles (Fig. 11) demonstrated that the average size of the silver particles obtained was approximately 30 nm. The resultant population showed a narrower distribution of sizes and shapes. It can also be concluded from the images that the particles obtained are quasi spherically shaped and do not tend to aggregate. Such conclusions are confirmed by analysis of the histograms shown in Fig. 11.

3.5 Examining the Stability of Silver Nanoparticle Suspensions

As it is known from the literature, the surface plasmon absorption and the fwhm depend on the aggregation of colloidal particles in the solution, and a higher absorption rate is caused by the growing amount of nanoparticles [41]. Therefore, the nanocolloidal silver suspensions obtained were monitored for stability. For this purpose, when the photoreduction of silver bromide crystals in a gelatine protection was over, the solution was stored in a sealed container to prevent the natural evaporation of the solution at room temperature (22°C). No further stabilisers were added to the post-reaction mixture, nor was the base-acid equilibrium of the solution changed. UV-Vis spectra of the stored solutions were performed three times, at different times: after finishing of synthesis, after 48 hours and after 48 days following the finish of silver nanoparticles synthesis. Based on the spectroscopic measurements, the spectral characteristics of silver nanoparticles were determined and presented in Fig. 12. If nanoparticles increase in

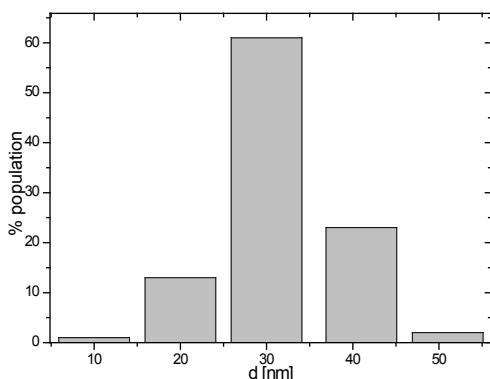


Figure 11. Size percentage distribution of silver nanoparticles resulting from the photoreduction of silver bromide crystals in the presence of ascorbic acid, estimated based on analysis of TEM photomicroographies.

size, then the maxima of spectral curves move towards the long-wave part of the spectrum [42]. No such effect was found in the results under review, which implies that the size of particles remains unchanged over time. The lack of change in the band shape and the absorption rate of nanocolloidal silver suspensions during their storage indicates that the properties of a nanoparticle population do not change from the completion of the synthesis for as long as it is stored at room temperature. Hence, it can be stated that the produced suspensions of colloidal silver feature a sufficiently high stability, which provides additional proof that the gelatine used as a protective colloid in the dispersion systems under review had good properties.

4. Conclusions

A method of using the photoreduction, in the presence of ascorbic acid as a reductant, to produce silver nanoparticles from ultrafine crystalline suspensions of silver bromide in a gelatine protection is described. It was suggested that silver particles could be produced by simultaneously applying both photochemical and chemical reduction of hardly soluble silver salt. Research was conducted to examine how various medium factors might affect the efficiency of AgBr photoreduction to nanostructural silver. Based on the experiments performed, it was found that the best results could be achieved by using ascorbic acid in a threefold molar excess compared with silver bromide, in a gelatine protection, with the presence of a small amount of sodium sulphite, at the reaction's pH of 10.0, a 60-minute reaction time and a two-minute photo-

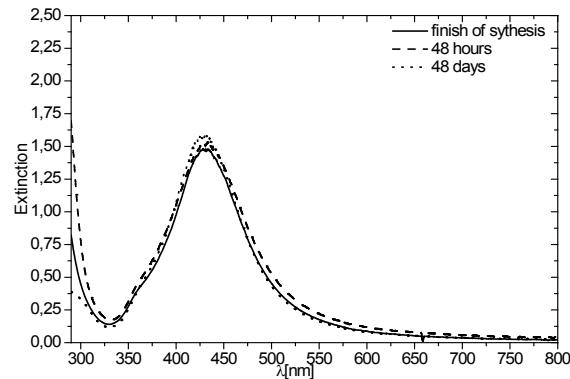


Figure 12. UV-Vis spectra of silver nanoparticles water suspension recorded after one hour, after 48 hours and after 48 days following the start of the synthesis.

initiation of the reduction process by exposure to radiation from the halogen lamp. The reaction carried out in the so defined physicochemical conditions was named characteristic, and it was used by the authors for further research into the production of silver nanoparticles using the method described above, which involves the photoreduction of silver bromide crystals doped with metals and/or sensitised spectrally. The presented method of obtaining nanostructural silver makes it possible to produce silver particles, featuring intense plasmon absorption at a wavelength of approximately 425 nm, in an easy and efficient way. You should pay special attention to the fact that the colloidal solutions obtained showed very high stability and reduced aggregation tendency, which was reflected in the lack of changes in the UV-Vis spectra from the sample stored at room temperature 48 days after synthesis. Dynamic Light Scattering analysis confirmed that the particles formed were quasi spherical in shape, with a majority of particles ranging from 15 nm to 30 nm in diameter.

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