Preparation and characterization of ultra-fine silver bromide suspension

Agnieszka Król-Gracz, E. Michalak, P. Nowak, A. Dyonizy

Wrocław University of Technology, Institute of Physical and Theoretical Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, e-mail: agnieszka.krol@pwr.wroc.pl

This paper present the results of studies on ultra fine-crystalline silver bromide suspensions, which were stabilized by gelatin and excess of bromide ions. Relation between dosing rate of reactants to size of obtained silver bromide crystals was investigated. Granulometric properties obtained nanocrystals were studied by turbidity method and by technique of Dynamic Light Scattering (DLS). Additionally, a photomicrograph of suspension using Scanning Electron Microscopy (SEM) was performed.

Keywords and phrases: nanoparticles, silver bromide, synthesis method, gelatine.

Introduction

The popularity and continuing growth of interest in nanoparticles due to their important role in the production of materials with specific chemical, physical and optical properties. Strongly developed nanometer size structures results in increased chemical reactivity of these individuals. An example this type of particles are silver halides, which are mainly use in: photographic materials, electrochemistry and photoelectrochemistry. They are used in production of photochromatic glass and in synthesis the composites with antibacterial properties [1–3]. Methods for obtaining nanocrystals of silver halides are many, the most popular ones are: microemulsion method [4] and precipitation of silver bromide nanoparticles in polymer matrices [5]. However, the populations generated by these methods have high particle size and shape distribution. Therefore, still conduct research on obtaining the monodisperse silver bromide crystal suspensions. The main obstruction in obtaining this type of suspension is their tendency to aggregate. Important in studies on obtaining this type of particle is the medium where these particles are synthesized.

In these research using photographic gelatin — a natural protective colloid, strongly impeding silver halide crystals formation. The degree of crystals formation retardance described by PAGI METHOD standards, PR value should not exceed 60. The use of gelatin, it also increases the environmentally friendly aspect of the research.

The main purpose of the presented experiments was preparing ultra fine-crystalline silver bromide suspensions with particle size and shape distribution as small as possible. Research was conducted using a method for synthesis of submicron suspension of silver bromide described in [6–7]. This method modified for obtaining silver bromide crystals as small as possible.

The authors use the obtained silver bromide crystals suspensions as a substrate in synthesis of silver nanoparticles by using photochemical reduction and mild, chemical reduction, resulting in metallic silver characterized by nanocolloidal dispersion.

Experiments

Preparing of ultra fine-crystalline silver bromide suspension depend upon alternating dose of water solutions of silver nitrate and potassium bromide introduce into dispersive solution, 100 ml 5% (weight) gelatin solution. Reagents are added in volume of 10 ml in 15-second intervals. The process was carried out throughout 10 cycles (single dose of silver nitrate and potassium bromide), in the concentrations 0.1–1.0 M (mol/dm^3). After finishing each full cycle of dosing, the crystalline system was set aside for 5 sec. to allow

homogenization and stabilization of physicochemical conditions throughout the whole reaction vessel. To obtain the smallest, possible thermodynamically stable crystal seeds, process was carried out at low temperature to 35°C. The overall time of process did not exceed 350 secs. Scheme of preparing of AgBr crystals suspension are illustrated in Fig. 1. The purpose of experiments was investigate the influence of substrates concentration on the average size of silver bromide crystals formed in the final stages of suspension synthesis. Synthesis such suspensions required the use of reagent in the following concentrations 0.1, 0.3, 0.5, 0.7 and 1.0 M.

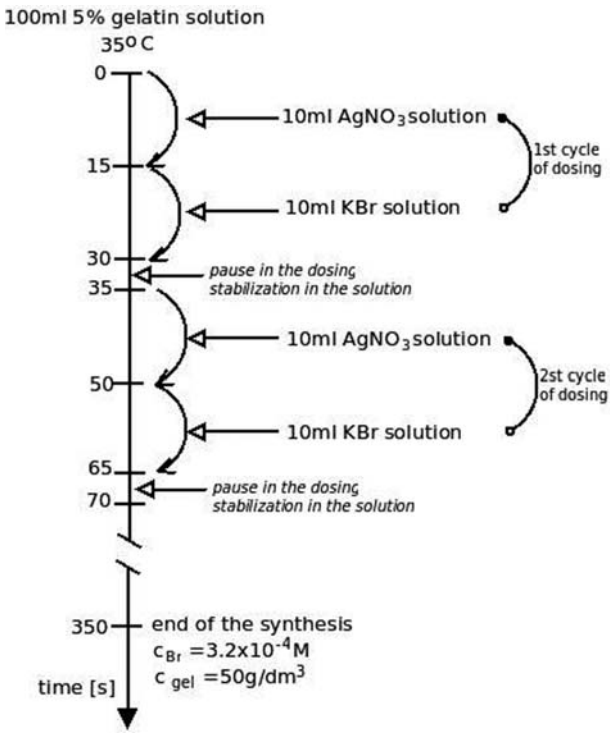

Fig. 1. Scheme of precipitation of silver bromide crystals suspension.

Additionally, the reaction vessel was equipped with a potentiometric measurement system, allowing for control of correctness of experiments by recording of bromide ions activity changes during the synthesis. During the experiment, after each cycles, the samples were collected in a volume of 1 cm^3, were diluted with distilled water and their spectral turbidity analysis were recorded. It consisted of the obtained turbidity on wavelength dependence function.

Towards the end of process, excess bromide ions concentration was stabilized at 3.2×10^{-4} M and the suspension was further stabilized by addition of gelatin in an amount 50 g/dm^3. After the dissolution of gelatin the suspension was ground mechanically and washed out with clean, cold water. Washing was stopped after obtaining salinity lower than 20 ppm. This treatment was performed to prevent recrystallisation of silver bromide crystals. The next stage of the experiment was regulation of excess bromide ions concentration to a value of 3.2×10^{-4}, it is a minimum solubility of silver bromide. Then the suspension was stored at temperature of 3–8°C.

The size of the crystals was determined base on the spectral turbidity dependences and the *Rayleigh's* relation (for example [8–9]). Calculated diameter of spherical particles of silver bromide crystals in the various suspensions, which were converted into the length of the edges of the cube (d_6) [10], because in this synthesis conditions obtained primarily cubic silver bromide crystals. The calculation was performed for the wavelength of light 600 nm. This wavelength was chosen to remove the influence self-absorption on measurements of silver bromide crystal, therefore far from the silver bromide self-absorption of 480 nm and to avoid errors associated with an unfavorable ratio of signal to noise limits sensitivity for the equipment.

Analysis of size and size distribution of silver bromide suspensions obtained after synthesis was performed using dynamic light scattering *DLS*. Additionally, an analysis scanning electron photo-micrographs were determined.

Results and discussion

Figure 2 illustrates selected curves of changing turbidity as a function of the light wavelength, recorded during the synthesis of AgBr suspension, from solutions of reactants of 0.1 M concentration. Each spectral curve corresponds approximately to the conditions present in the reaction mixture at the end of each 10 dosing cycles. The increase in turbidity of the mixture of crystallization occurs after each dispensing cycle, because a number of stable silver bromide crystals formed and their size varies slightly during the synthesis.

Very small silver bromide crystal seeds are thermodynamically unstable, therefore they are dissolved, and its mass deposited on the larger crystals. Completion of each dispensing cycle leads to the stabilization of the size and the number of crystals, this fact favors the formation of almost monodisperse ultra fine-crystalline silver bromide sols. The results of experiments were confirmed by calculations carried out using self-developed procedure, based on *Rayleigh's* scattering theory, used to estimate the size and number of AgBr crystals forming in the mixture after each cycle of crystallization reagents dosage. Established theory of *Rayleigh's* scattering and the resulting dependence quoted in [11], presented at the conference last year's *Young Scientists Towards the Challenges of contemporary technology*.

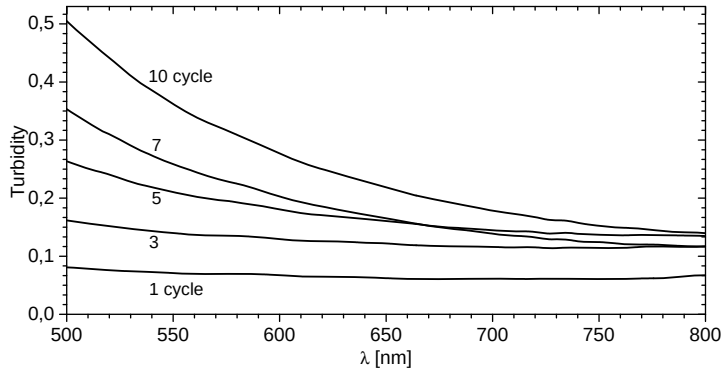

Fig. 2. An example of turbidity changing, recorded during precipitation of silver bromide crystals suspension of, from solution of reactants of 1.0 M concentration.

Based on recorded turbidity in crystallization mixture and calculations made, determined changes in crystal size of silver bromide expressed by the edge of the cube (d_6), as a function of cycle dosing of reagents, as shown in Fig. 3. Results of calculations of average size d_6 were presented for the same cycles of dosing, which is illustrated in Fig. 2. It was noted that the increase in crystal size after each delivery of reagents to the reaction medium is linear, which confirms the assumption that in the environment after each cycle of crystallization similar thermodynamic conditions prevail. The results show a good linear correlation (R = 0.98) and the equation is:

$$d_6 = 23.9 + 2.6 \times \text{number of dosing cycle} \qquad (1)$$

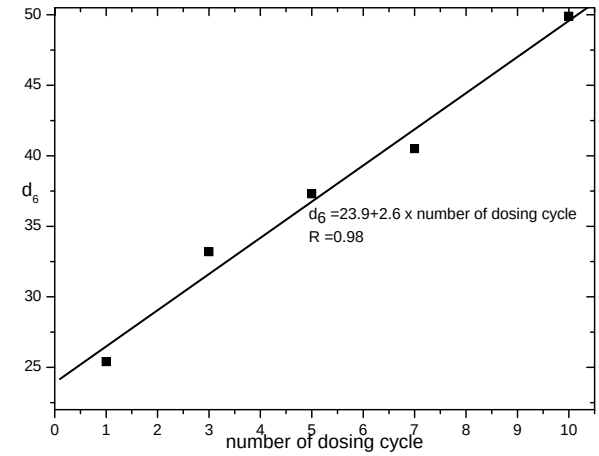

Fig. 3. Relation between the average size of AgBr crystals in selected stages of the synthesis, from solution of reactants of 0.1 M concentration, calculated at the wavelength 600nm, as a function of the number of dosing cycle.

For each suspension of silver bromide nanocrystals after synthesis, the size and size distribution by dynamic light scattering DLS were studied. Measurements were done for the laser light source with a wavelength of 532 nm at a constant temperature of 22°C. This technique, known as photon correlation spectroscopy PCS, can be used to determine the size distribution of crystals in the dispersion system containing a particle size ranging from 1 nm to 1 μm. Shining a monochromatic light beam, such as a laser, onto a solution with spherical particles in Brownian motion causes a Doppler Shift when the light hits the moving particle, changing the wavelength of the incoming light. This change is related to the size of the particle. It is possible to compute the sphere size distribution and give a description of the particle's motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function.

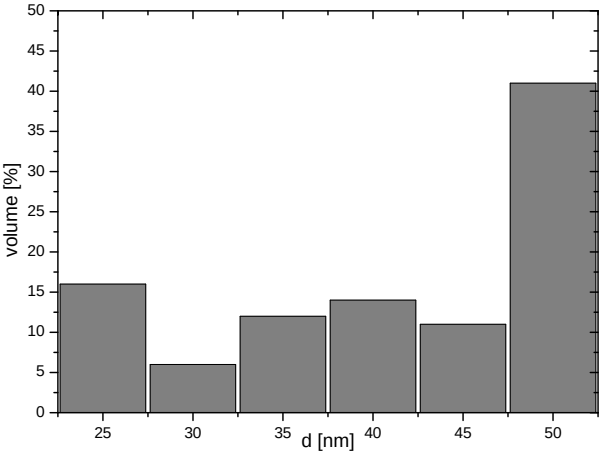

Fig. 4. Volume size distribution of AgBr crystals suspension, from solution of reactants of 0.1 M concentration.

Based on DLS measurements, graphs according to the percentage volume occupied by particles of a certain diameter found in the study population were drawn up. Result for the AgBr crystals suspension, from solutions of reactants of 0.1 M concentration are presented in Fig. 4. In the total population is dominated crystals with a diameter of about 50 nm, but it is also evident in the dispersion of size 27–50 nm. For the remaining suspensions size dispersion and main size of silver bromide nanoparticles obtained are shown in Table 1.

Table 1. The size of silver bromide crystals suspension, from solution of reactants in range from 0.1 to 1.0 M.

Concentration of reactants	Dispersion of size [nm]	Main size d6 [nm]
0.1 M	27–50	50
0.3 M	30–54	53
0.5 M	30–60	58
0.7 M	35–63	60
1.0 M	48–68	65

After spectrophotometric studies were carried out for selected concentrations of the reactants with a value of: 0.1, 0.3, 0.5, 0.7 and 1.0 M, determined changes in the size of cubic silver bromide crystals obtained in the final stage of synthesis. Relation between the average size of silver bromide crystals as a function of the concentration of reactants (C_r) in a mixture is shown in Fig. 5. The results obtained were fitted with straight line, obtaining the value of correlation R = 0.99. Thus obtained a good linear correlation, explains that in terms of changing concentrations of reactants in the range from 0.1 to 1.0 M, the size of silver bromide crystals, which are formed during the synthesis of a suspension of AgBr, depends linearly on the concentration of the reactants and the speed mass dispensing of reagents. Similar results were obtained for a wider range of concentrations of 0.5–3.5 M, as described in [11].

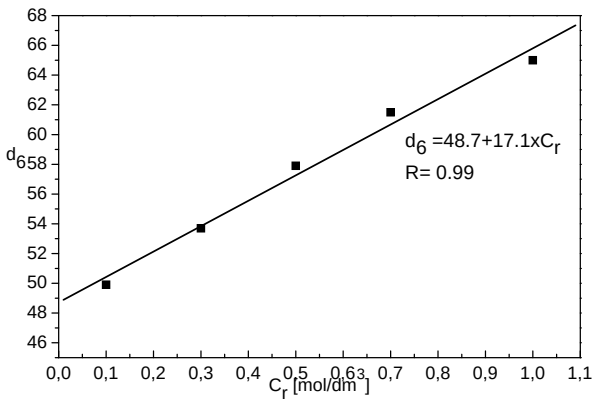

Fig. 5. Relation between the average size of AgBr crystals, calculated at the wavelength 600 nm, as a function of the concentration of reactants solutions.

The size of silver bromide nanoparticles was confirmed by the analysis of images taken using a scanning electron microscope SEM, which shows a sample photomicrograph (Fig. 6). The average crystal size in this population is 65 nm. The results of these measurements are consistent with the results obtained by spectroscopic measurements and dynamic light scattering.

Conclusion

Using spectrophotometric method in the study on granulometric characteristics of the final suspension, allows to obtain information about the average size of synthesed structures, using simple measurement tools and self-developed computational procedures. The results were confirmed by spectroscopic analysis of images obtained by scanning electron microscopy technique and the method of dynamic light scattering, which justifies the correctness of the application of spectroscopic methods, the use of which is cheaper and less time consuming.

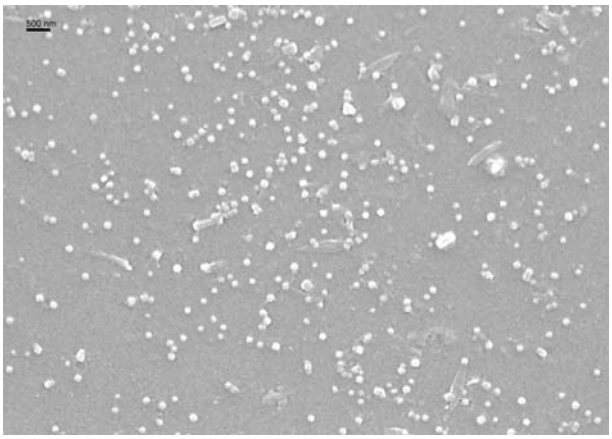

Fig. 6. SEM image of AgBr crystal suspension, from solution of reactants of 1.0 M concentration.

Based on experiments performed, it was noted that lower concentrations of the reactants used for synthesis of silver bromide suspensions receiving favors smaller silver halide crystals. Crystals located in the scale of nanostructures, with less than 100 nm in size, are obtained with concentrations of aqueous solutions of potassium bromide and silver nitrate of less than 2.5 M [11]. In order to receive ultra ultra-crystalline crystals suspensions, whose final size would be below 50 nm should be used concentrations of substrates below 0.1 M. The disadvantage of this solution is a relatively low final concentration of silver bromide, which in turn makes it difficult to obtain concentrated nanosols of silver, with a more utilitarian use.

Currently, the authors lead the work on the possibility of application of research methodology developed in the work associated with the production silver nanosols. We successfully use the substrate in the form of ultra fine-crystalline of silver bromide crystals suspensions to receive the silver nanoparticles by photochemical and / or chemical reduction of light-sensitive silver salt.

Acknowledgements:

The authors would like to acknowledge Mr. T. Koźlecki for the opportunity to make analysis by dynamic light scattering method in the Department of Chemical Engineering University of Technology.

Sources of funding

The scientific work is financed by the school in 2010--2011, as the research project N N508 488938th.

References

[1] Lanz, M., D. Schürch, and G. Calzaferri. "Photocatalytic Oxidation of Water to O_2 on AgCl-coated Electrodes". *J. Photochem. Photobiol. A: Chem* 120 (1999): 105–117.

[2] Tomonaga, H., and T. Morimoto. "Photochromic coatings including silver halide microcrystals via sol-gel process". *Thin Solid Films* 392 (2001): 355–360.
[3] Sambhy, V., et al. "Silver Bromide Nanoparticle/Polymer Composites: Dual Action Tunable Antimicrobial Materials". *J. AM. CHEM. SOC.* 128 (2006): 9798--9808.
[4] Monnoyer, Ph., A. Fonseca, and J.B. Nagy. "Preparation of colloidal AgBr particles from microemulsions". *Colloids Surfaces A: Physicochem. Eng. Aspects* 100 (1995): 233--243.
[5] Liu, X.-H., et al. "A novel cetyltrimethyl ammonium silver bromide complex and silver bromide nanoparticles obtained by the surfactant counterion". *Journal of Colloid and Interface Science* 307 (2007): 94–100.
[6] Thiry, H. "Preparation and properties of ultra fine grain AgBr emulsion". *J. Photogr. Sc.i.* 35 (1987): 150–154.
[7] Zaleski, A., P. Nowak, and J. Węglińska-Flis. Politechnika Wrocławska. PL192773. 15.12.2000.
[8] Berry, C.R. "Turbidity of monodisperse suspensions of AgBr". *J. Opt. Soc. Am.* l, 52, 8 (1962): 888–895.
[9] Zaleski, A. "Some aspects of crystal growth in the double--jet method of photographic emulsion preparation". *J. Photogr. Sci*. 27 (1979): 43–46.
[10] Dyonizy, A., et al. "Synthesis of silver bromide ultra fine--crystalline suspension". *CHEMIK* 64(1), 2010: 33–44.
[11] Król-Gracz, A., et al. "Size-controlled synthesis of silver bromide nanoparticles", *Young scientists towards the challenges of contemporary technology.* Warszawa 2009: 394–400.