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Hydroquinone Synthesis of Silver Nanoparticles from Silver Bromide Suspensions

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The results of research into the preparation of silver nanoparticles using photoreduction in the presence of hydroquinone as the reductant were discussed. Substrates for the synthesis of silver nanoparticles were ultrafine crystalline gelatine-stabilised aqueous suspensions of silver bromide. The influence of the reductant to substrate molar ratio and the medium's pH to the efficient production of silver nanoparticles were studied. The properties of resultant silver particles were examined using UV-Vis spectroscopy. Transmission electron microscopy was used for the photomicrography of silver nanoparticles suspensions.

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1. Introduction

Silver nanoparticles (Ag NPs) have considerable interest among scientists due to their remarkable properties: antibacterial, catalytic and specific physical and optical properties [1–4]. The use of materials that have silver nanoparticles in their structure includes but is not limited to cosmetics, pharmaceuticals, clothes and in designing solar cells [5–7]. In the last years plenty methods of synthesis for the preparation of Ag NPs have been reported [8–12]. Silver nanoparticles are most often synthesised using chemical reduction. It is silver nitrate and silver perchlorate that are 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 (e.g. [13]). Another method of obtaining nanostructured silver is a photolysis of silver salts. The colloidal particles can be achieved and the reduction of metal ions can be controlled through the control of the exposure time with the photolysis [14].

The following paper presents a method for obtaining silver nanoparticles by photoreduction of ultrafine crystalline gelatine-stabilised suspensions of silver bromide. Photoreduction is the combined method, which merges the photolysis and the chemical reduction. Silver nanoparticles are obtained with applying actinic radiation and chemical reductant. An advantage of using 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 lets silver ions be released slowly to the medium, making it quite easy to control the crystallisation of nanostructural silver. Hydroquinone (HQ) was applied as reducing agent. Silver ions are reduced with hydroquinone in a molar ratio of 2:1, with a surplus of silver ions [15].

This study presents the photoreduction of silver bromide with an initiation by electromagnetic radiation which enables to obtain doped centers in the form of silver clusters on the surface of silver bromide crystals. At a later stage of reduction silver clusters are converted into silver nanoparticles in the presence of hydroquinone. It is shown that hydroquinone in the gelatine medium and slightly basic pH is an effective reducing agent used for the preparation of Ag NPs only when the reduction reaction was initiated with light. The paper discusses the influence of the reductant to substrate molar ratio on the efficient production of silver nanoparticles.

2. Experiment

The reactions were staged in a special darkroom with dark red protective lighting. Suspensions of silver bromide crystals (average diameter 60 nm) were used as a substrate for the synthesis of nanoparticles silver. Ultrafine silver bromide suspensions were obtained using method which is described by Dyonizy et al. [16]. 1 ml of 0.333 M silver bromide crystal suspension was put into a reaction vessel in the form of a 100 ml large quartz cuvette, which was then diluted with water down to 70 ml. Sodium sulphite was added subsequently, in order to prevent the oxidisation of hydroquinone of oxygen and hydroquinone as the reducing agents. The whole 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 0.5 g/dm^3 . The experiments were conducted with a 2 minute exposition using a halogen lamp (1000 W POLAM LH21) of the reaction mixture, which was being stirred vigorously throughout the whole process of synthesis. The distance of the cuvette from the source of electromagnetic radiation was 20 cm. UV-Vis spectra were generated using an Ocean-Optics USB-4000 fibre optic spectrometer. Transmission electron microscopy (TEM) photomicrographies were made using FEI Tecnai G2 20 X-TWIN microscope,

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with an accelerating voltage of 120 kV. Microscope specimens were prepared by depositing the carbon-coated copper grids. The study used analytical purity reagents manufactured by POCH S.A. Poland.

3. Results and discussions

Photoreduction was conducted in the presence of actinic radiation or absence of light during the reduction of ultrafine silver bromide suspensions. Hydroquinone was used as the reductant. The impact of the reductant to silver bromide molar ratio: 0.32, 0.62, 1.60 and 3.10 in the medium of constant pH of 8.7 was examined. Fig-

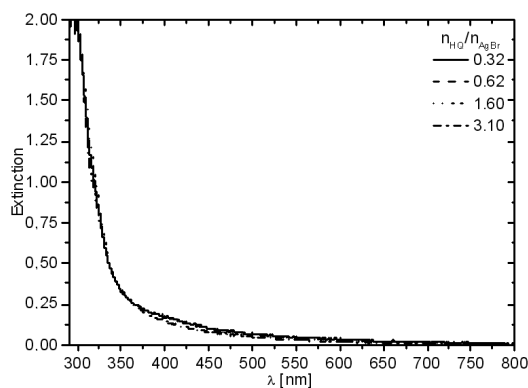


Fig. 1. UV-Vis spectra of silver nanoparticles recorded after 20 h of the reduction of AgBr crystals in the presence of hydroquinone and without exposition to light. Molar ratio of HQ to AgBr was: 0.32, 0.62, 1.60, and 3.10.

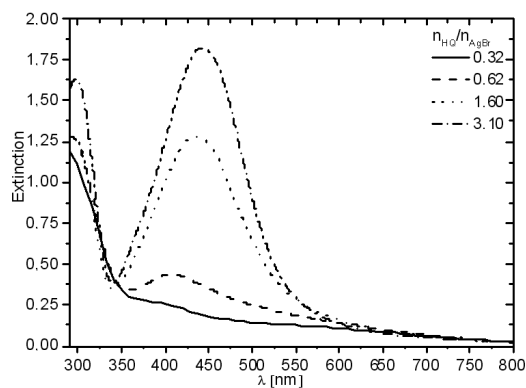


Fig. 2. UV-Vis spectra recorded after 20 h of the photoreduction of AgBr crystals in the presence of hydroquinone with 2 min exposition to light. Molar ratio of HQ to AgBr was 0.32, 0.62, 1.60, and 3.10.

ure 1 presents the UV-Vis spectrum obtained after 20 h of silver bromide crystals suspensions reduction in the presence of hydroquinone, without exposition to light. It was found that the reduction of ultrafine silver bromide crystals almost do not exist in the studied molar ratios of reactants and pH 8.7 despite the fact the pH

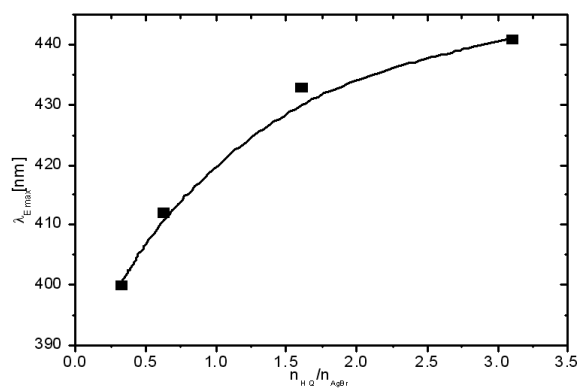


Fig. 3. Position of an extinction band maximum of the Ag NPs obtained in different molar ratio of HQ to AgBr after the photoreduction with exposition to light.

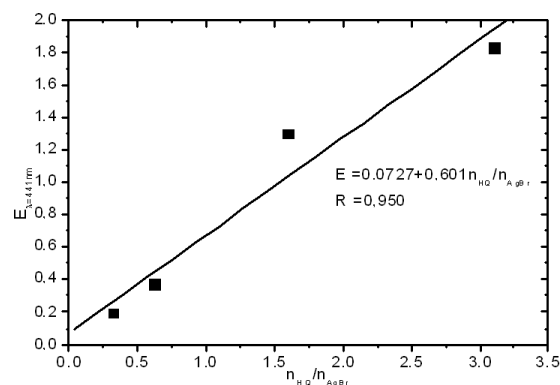


Fig. 4. Maximum extinction of the Ag NPs obtained in different molar ratio of HQ to AgBr after the photoreduction with exposition to light.

limit in which the hydroquinone reaches a sufficiently low oxidation-reduction potential to reduce the silver bromide is 7.9 [17]. The probable reason for the lack of reduction reaction in the absence of light, pH 8.7, in the presence of gelatine is too high value of the oxidation-reduction potential barrier at which the hydroquinone does not 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 hydroquinone.

Figure 2 shows the spectral dependence obtained after 20 h of photoreduction of silver bromide suspensions in different molar ratio of hydroquinone to the substrate and a constant pH of 8.7. This process was initiated by 2 min exposure to light of the reaction mixture. Silver nanoparticles obtained at a molar ratio of reductant to AgBr: 0.32, 0.62, 1.60, and 3.10 present the maximum extinction at a wavelength of 398, 410, 436, and 440 nm, respectively (Fig. 3). The extinction peaks shifted to longer wavelength and became narrower with the elevated molar

ratio, possibly due to decreased dispersion of size obtaining silver nanoparticles [18]. The plasmon effect, which is typical of spherically shaped Ag NPs, occurs in range from 390 to 440 nm, relating to size distribution from 4 to 50 nm [19]. When reductant amount increased in the reaction medium, we observed extinction maximum increase in the range of 0.2 to 3-fold excess AgBr relative to HQ and the HQ of 1.8 for the 3-fold excess of reductant

in relation to the substrate (Fig. 4). The results show a good linear correlation with $R = 0.950$. Hydroquinone reduction of silver bromide occurs at 2-fold excess of silver bromide stoichiometrically but reactions carried out in similar conditions ($n_{\text{HQ}}/n_{\text{AgBr}} = 0.62$) was relatively ineffective. Photoreduction reaction at a pH of 8.7 was most effective in three excess of hydroquinone (Fig. 2).

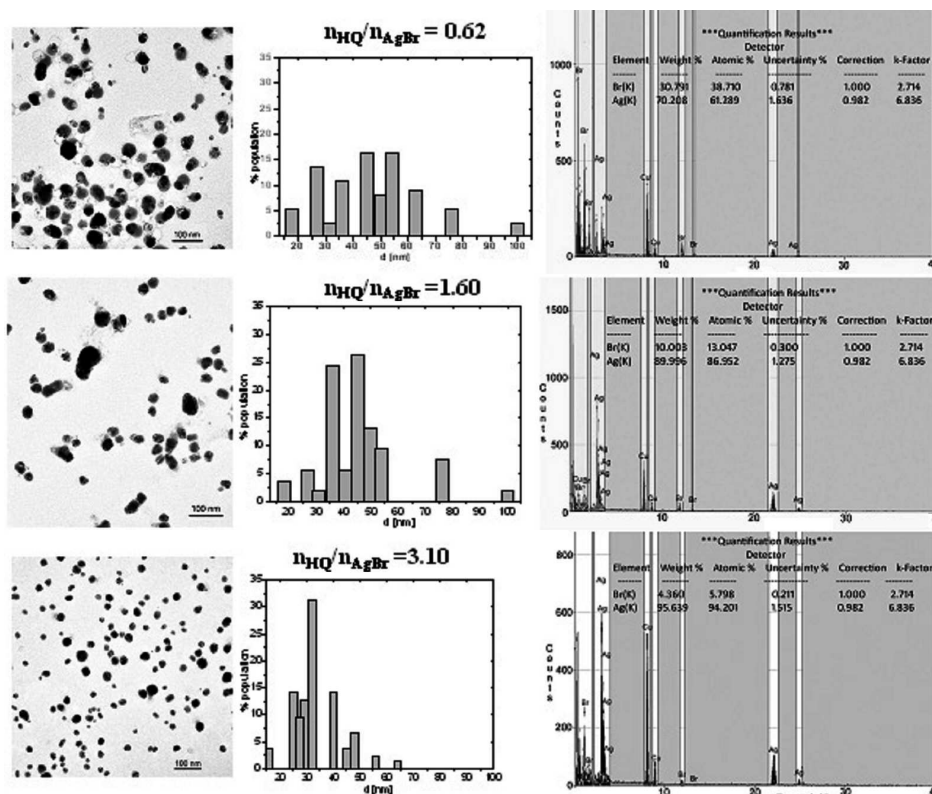


Fig. 5. TEM photomicrographs, size percentage distribution and EDX spectrum of resultant silver nanoparticles obtained using the photoreduction in the presence hydroquinone.

Analysis of the photomicrographs obtained using the TEM method and of chemical composition the energy dispersive X-ray (EDX) of silver nanoparticles (Fig. 5) demonstrated that the growth of molar ratio of hydroquinone to silver bromide causes decrease of average size of silver nanoparticles obtained and decrease the amount of unreacted silver bromide in the range of 30% for the molar ratio of HQ to AgBr 0.62 to 4.4% for the 3-fold excess of hydroquinone. Population of silver particles obtained in molar ratio reductant to AgBr of 3.10 has a smaller size and shape dispersion of silver particles than silver obtained in excess of AgBr as evidenced by the size distribution histograms of silver nanoparticles (Fig. 5). The population of silver nanoparticles obtained at the molar ratio of AgBr to HQ 0.62 characterized by the dispersion of particle size from 16 nm to 100 nm but was dominated by structures with a diameter of 45 nm and

54 nm. The resultant population prepared in the 1.6-fold excess of reductant to the substrate was in the size range 18 nm to 100 nm but with the dominant population of silver by 35 nm and 45 nm in diameter. The most monodisperse of silver nanoparticles was obtained in the population of 3-fold excess of hydroquinone to AgBr, the average size of silver particles obtained was approximately 30 nm. It can also be concluded from the TEM photomicrographs that the particles obtained are spherically shaped and do not tend to aggregate.

4. Conclusions

Described is a method of using the photoreduction, in the presence of hydroquinone as the reductant, of ultra-fine crystalline suspensions of silver bromide in a gelatine protection to obtain silver nanoparticles. The paper discusses the influence of the reductant to substrate molar

ratio on the efficient production of silver nanoparticles. We show that HQ is unable to reduce isolated silver ions but is able to reduce the same ions when added onto pre-existing silver metallic clusters. In this study we show that UV radiation can be used to initiate the HQ reduction of AgBr and then the radiation can be removed to allow HQ to finish the Ag NPs growth on its own in dark. TEM analysis confirmed that silver particles formed were shaped almost spherically, with a majority of structures ranging from 15 nm to 65 nm in diameter. Tests performed using a spectrometer indicated that it is possible to obtain silver nanoparticles with their maximum extinction rates ranging from 400 to 440 nm. The plasmon effect, which is typical of spherically shaped silver nanoparticles, occurs in this range. The presented method of obtaining nanostructural silver makes it possible to produce silver particles, featuring intense plasmon absorption at a wavelength in the range from 400 nm to 440 nm, in an easy and efficient way. The resulting colloidal silver has the shape close to spherical and has no tendency to aggregation.

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