

Production of silver nanoparticles in water solution by radiation treatment

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Abstract. Radiation-chemical synthesis of silver nanoparticles was studied. The silver nanoparticles in arabinogalactan (AG) water solution are stabilized in conglomerates, it is fixed by rise of additional bands in the optical absorption spectra. Pre-radiation treatment of AG causes crosslinking and oxidation. Pretreated AG solution increases the stability of conglomerates containing silver nanoparticles in case of dilution.

1. Introduction

The aqueous solutions containing silver nanoparticles are now used in medical practice, and their applications are widening. Production of stable water solutions containing silver nanoparticles is important both for theoretical and practical considerations. It is witnessed by numerous works [1]. Water-soluble polymers, including natural biopolymers, added into water are efficient stabilizers of silver nanoparticles [2]. Natural biopolymers can favor to form nanoparticles having narrow size distribution perhaps due to solution structuring and formation of permolecular structure. Natural polymers can have some advantages, for example, they can simultaneously be deoxidizers for silver ions and stabilizers for resulting dispersions. Other important properties of natural biopolymers are biocompatibility and low toxicity.

Arabinogalactan (AG) is biocompatible branched natural polysaccharide that can act both as deoxidizer and stabilizer. Beside these AG is capable to structure on its own into globules of various sizes depending on concentration in solution [4].

Publication [5] describes deoxidizing properties of the AG, a highly alkaline medium was used to activate it. Silver or silver hydroxide precipitation in alkaline medium is inevitable, and a reaction localization (in solution or heterogeneously on sediments' surface) is not known. Alkaline infusion for activation of AG deoxidizing properties can also be regarded as chemical deoxidizing.

Chemical deoxidizing methods for silver nanoparticles formation lead to product pollution. It restricts application of reaction product or requires additional stages to remove intermediate products. And presence of chemical deoxidizer influences on stabilization and self-organization processes. A work [6] shows that silver nanoparticles formed in photochemical deoxidizing process are ordered on nanocarbon tubes functionalized by sodium dodecylphosphate, and collective photon effects are



displayed. A chemical deoxidizing resulted in chaotic nanoparticles arrangement on carbon nanofibers.

Another way to produce metal nanoparticles without chemical deoxidizers is radiation-chemical process [7]. Powerful ionizing radiation required for this process can be generated either by unstable isotopes or by electron accelerators. Advantages of modern electron accelerators as radiation sources are high radiation intensity, possibility of operative process control and high reproducibility [8]. Radiation treatment can be done by electron beam or by X-ray generated by special converter [9]. Metal ions deoxidization during water solutions irradiation can be done by water radiolysis products [10] and perhaps by free electrons.

Aim of our work was to study electron beam treatment possibilities for production of stable water solutions containing silver nanoparticles and AG as a stabilizer. Dependence of solution properties on preliminary AG solution electron beam treatment was studied, it was compared with AG solution without preliminary electron beam treatment.

2. Experiment

Arabinogalactan ($M_r = 17,000$ by GPC) was separated out of larch wood (*Lárix sibirica* Ledeb.) [11]. 0.01 M AgClO_4 water solution in 0.05M HClO_4 aqueous solution was produced by silver oxide powder (product of extra pure grade AgNO_3 thermal decomposition) dissolving.

Reaction solutions electron-beam treatment was carried out by pulse linear electron accelerator ILU-6 (BINP SB RAS). The electron energy was 2.4 MeV, beam pulse current was 320 mA, pulse repetition rate was 5 Hz, pulse duration was 0.5 ms and average beam current was 0.45 mA.

Solutions were treated in polytetrafluoroethylene containers. The solution layer thickness was up to 5 mm. Containers with solutions accumulated required doses by multiple passing under accelerator beam window at a speed of 2 cm/sec, dose per pass was 5 kGy. Intervals between passes were about 30 seconds. 5 minute time breaks were inserted after every 5 passages (dose of 25 kGy) to prevent excessive solutions heating up.

Preliminary AG electron beam treatment was done in 5% water solution, doses were 25, 50 and 75 kGy.

Silver nanoparticles were produced in water solutions containing 2.5% AG and 0.005 M of AgClO_4 (pure silver concentration was 0.535 g/l). This solution was treated with dose of 100 kGy.

UV-spectra were obtained by using a Cary-50 spectrophotometer (Varian). The absorption spectra were recorded within 1 day after the electron-beam treatment, solutions were placed in quartz cuvettes with absorbing layer of 1 cm. The solutions were diluted in 20, 40 and 320 times, see Figure 1.

The microstructure, phase structure, elemental and chemical composition of local sites were fixed by microscopic observations using

- TEM - JEM-2100 (Jeol, Japan) with addition of energy dispersive X-ray analysis (EDXA) on analyzer Inca-250,
- SEM - S-3400M (Hitachi, Japan) with the possibility of a local elementary analysis.

Solutions containing nanoparticles were placed on aluminum substrate and dried at ambient conditions. The final water removal from samples was carried out under reduced pressure.

Molecular weight distribution of the samples was determined by gel-permeation chromatography(GPC) on an Agilent 1200 chromatograph with a 1260 Infinity refractive-index detector (30°C, PL aquagel-OH 40, 300x7.5 mm, 0.1 M LiNO_3 , 1 ml/min). The column was calibrated using standard dextran samples (Sigma-Aldrich). The samples were studied as 0.2% weight solutions in 0.1 M LiNO_3 prepared using ultrasound.

3. Results and discussion

Just after electron beam treatment the treated solutions acquired dark red color that after storage during some hours changed into orange-red. The formed solutions contacting silver nanoparticles were stable during many months – no nanoparticles precipitation was fixed.

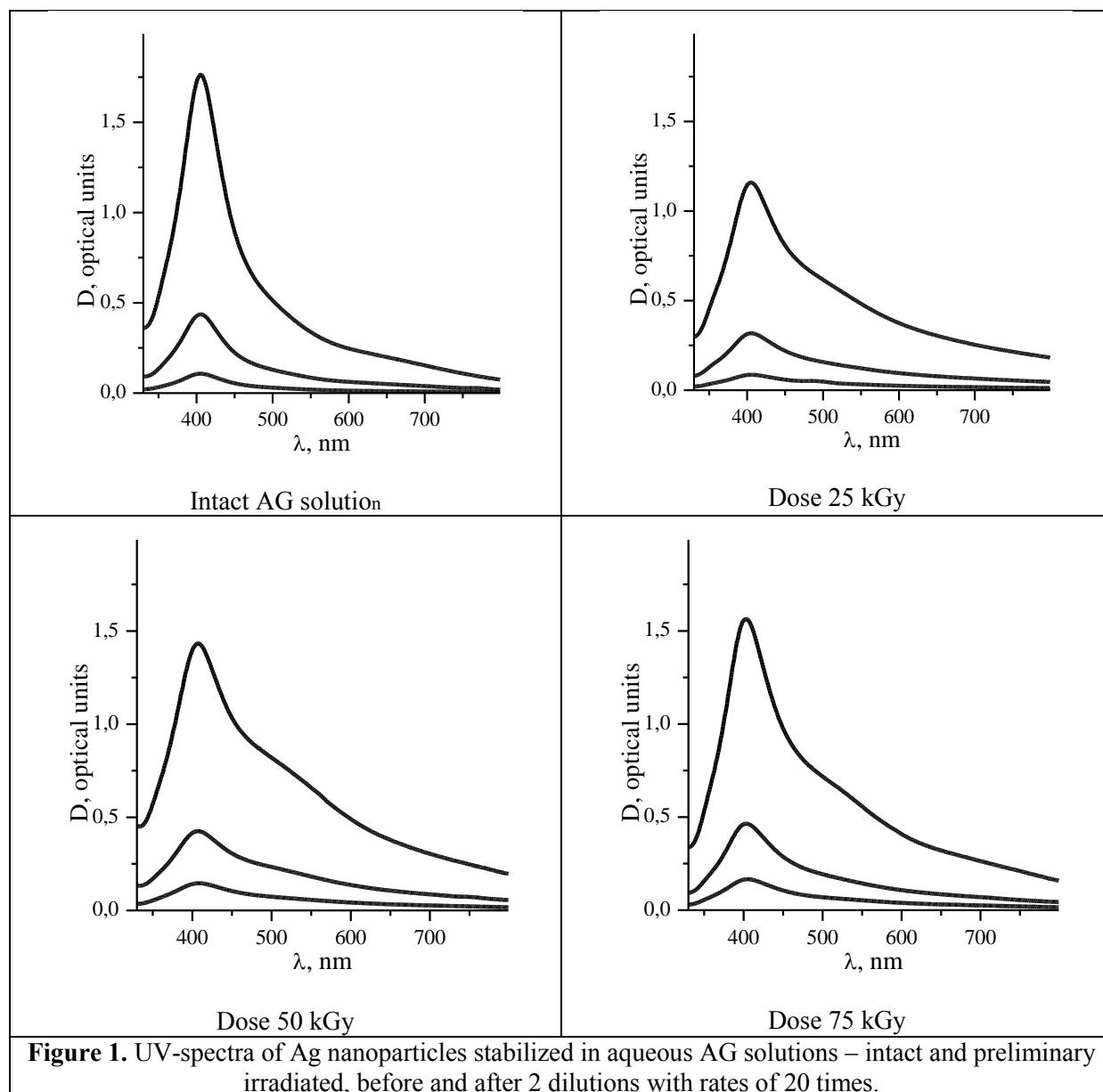


Figure 1. UV-spectra of Ag nanoparticles stabilized in aqueous AG solutions – intact and preliminary irradiated, before and after 2 dilutions with rates of 20 times.

Figure 1 shows optic absorption spectra of the silver nanoparticles in intact AG aqueous solution and in preliminary treated solutions with doses 25, 50 and 75 kGy before and after 2 dilutions having rates of 20 times. Absorption spectrum peaks in all cases is in region 403-407 nm. The spectra's forms are practically the same for all samples.

All spectra after dilution in 20 times show sufficient absorption in the region of more than 500 nm. Spectral factorization in coordinates optical density – frequency (reciprocal number, cm^{-1}) using Gauss method gave us 3 main spectral components with peaks in 400-410, 515-520 and 640-660 nm ranges.

Presence of some longitudinal plasmon resonances (LPR) in absorption spectra can be stipulated by some reasons [2,12]:

- presence of particles having sizes of more than 50 nm that leads to sufficient increase in quadruple component input into LPR;
- presence of faceting or great anisotropy in crystals' forms;
- particles' self-organization effects.

Last variant is most probable in our case as the dilution of AG solution without preliminary radiation treatment leads to practical disappearance of absorption in the region of higher than 500 nm.

The dilution of AG solution preliminary treated by radiation did not result in absorption disappearance in the range of 510-520 nm even after dilution in 1680 times.

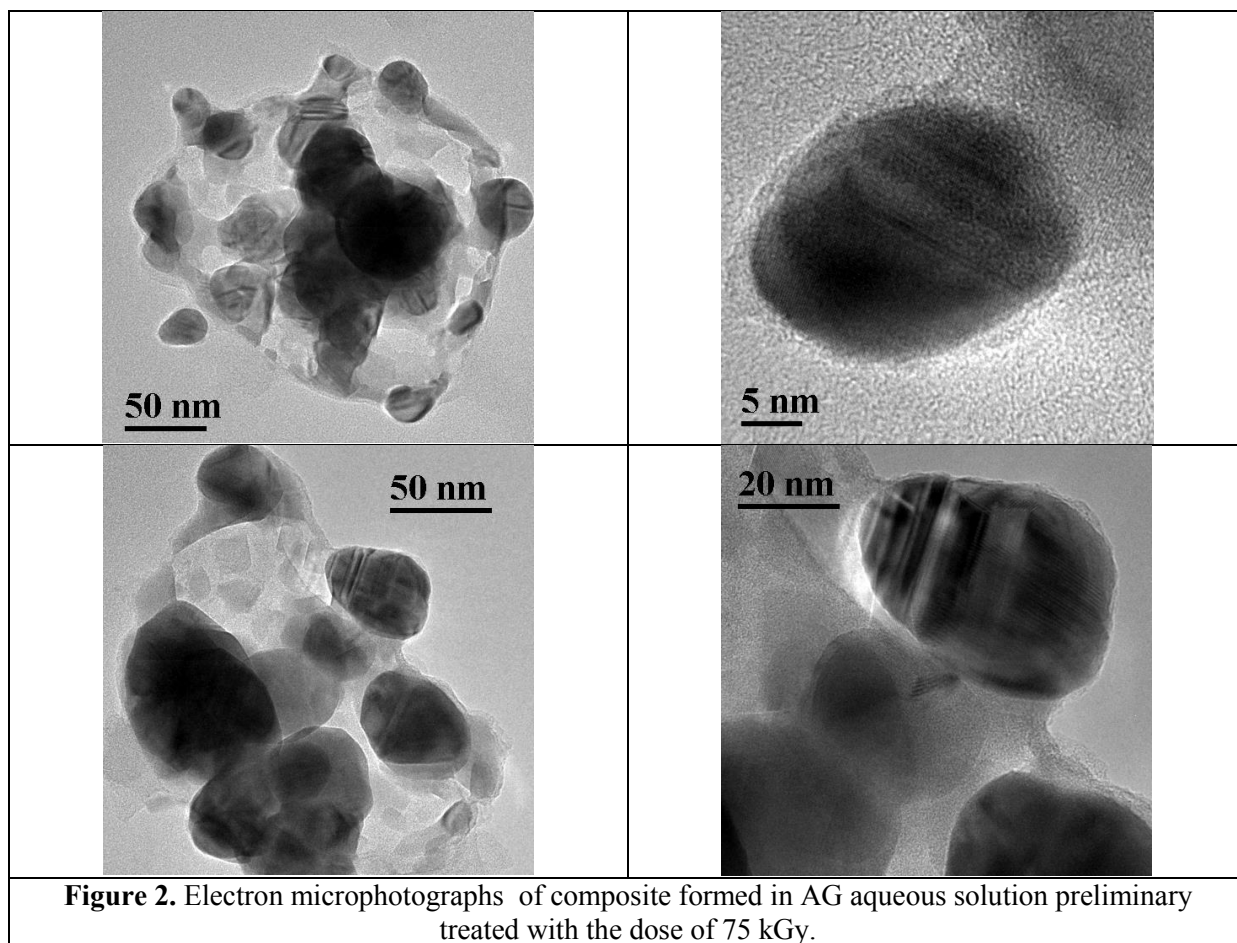
Electron microscopical study of films formed by solutions evaporation has shown that their surfaces are homogeneous. Particles of more dense material appeared after partial polymer matrix burning out by electron beam, element analysis confirmed that they are silver particles. Some particles with sizes less than 100 nm have low aspect correlation and form clusters with sizes up to 500 nm.

Nanoparticles' vicinity in the clusters engenders additional plasmon resonance lines like in [6]. Separate nanoparticles are practically not fixed conforming hypothesis about ordering.

High resolution electron microscopy images shown in Figure 2 witness presence of circular silver nanoparticle clusters. Big nanoparticles are located mainly on surface. These pictures correspond with earlier published data about AG water solutions gained by terahertz radiation. It was fixed that water solution AG concentration increase up to 1% results in globule size increase up to 75-80 nm. Concentration increase over 1% results in agglomeration of the formed globules [13].

Comparative experiments with water and dimethyl sulfoxide as solvent demonstrated that hydrogen bonds plays a decisive role in AG agglomeration [5].

So we consider the radiation-chemical silver nanoparticle synthesis results in nanoparticles stabilization due to fastening on the AG agglomerates' surfaces.



AG practically did not manifested its deoxidizing properties in chosen conditions of radiation-chemical silver reduction. Radiolysis reduction rate is higher than chemical reduction rate.

Nevertheless there is possibility that nanoparticles nuclei were formed and fastened on globules' surfaces during the process of AG and AgClO_4 reaction solutions preparation.

The AG aqueous solution electron beam treatment results in partial AG oxidation and crosslinking. 3-dimensional crosslinked gels formation was not observed after treatment of 2.5-10% aqueous AG solutions. AG is oxidized during irradiation by water radiolysis products, but differently than by classical peroxide oxidation [14]. Sedimentation by acetone carried out in 2.5-10% AG solutions after electron beam treatment with doses up to 150 kGy similarly as in [14] demonstrated low (less than 1%) low molecular weight fraction share. The classic peroxide oxidation gives low molecular weight fraction share up to 10%.

Probably AG is oxidized during irradiation like dextrans [15], and in classic dextran oxidation by potassium permanganate [16, 17] C-C bond breakages are going in pyranose and furanose rings without sufficient polymer chain cracking.

Figure 3 shows mass-molecular distributions of AG isolated from intact and irradiated 5% aqueous solutions.

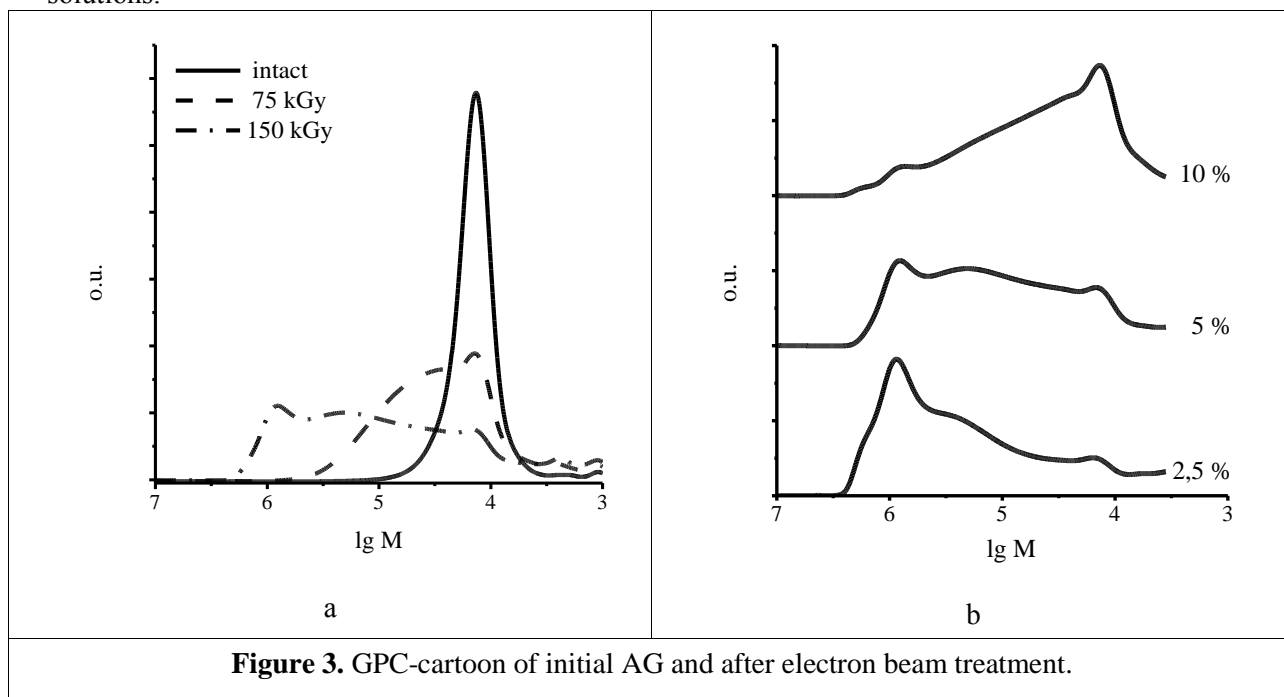


Figure 3. GPC-cartoon of initial AG and after electron beam treatment.

GPC studied had shown that AG solutions electron beam treatment resulted in MMP dispersion increase and sufficient molecular weight growth up to values of more than 1000000 ($\lg M = 6$). Maximum crosslinking rate was observed in low concentration AG solutions (Figure 3b, dose 150 kGy). Chromatograms of irradiated AG 2.5-10% solutions had initial AG peak witnessing reaction incompleteness. It can be caused by heterogeneity of system.

4. Conclusion

The formed solutions contacting silver nanoparticles were stable during many months – no nanoparticles precipitation was fixed. The following dilutions up to 1680 times does not cause the silver nanoparticles precipitation.

The data get earlier and our studies results show that AG solutions can be regarded as heterogeneous systems with ordered globules. The ordered nanoparticles clusters with small distances between them can be formed on their surfaces and it is stimulating cooperative effects. Perhaps the nuclei of the nanoparticles are forming during the reaction mixtures preparation.

Preliminary AG solutions irradiation results in formation of greater molecules and probably in formation of groups capable of strong hydrogen bonds formation. It helps to preserve AG conglomerates in solutions after dilutions.

The radiation-chemical reduction of silver aqueous AG solution leads to silver nanoparticles ordering. The appearance of additional absorption band in UV-spectra is due to the close proximity of the silver nanoparticles in these structures. The AG cross-linking and oxidation are going during electron-beam treatment. Preliminary electron beam treatment of aqueous AG solution improves conglomerated silver nanoparticles stability, and dilution in 1680 times does not cause the silver nanoparticles precipitation.

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