

NANOSILVER PREPARATION BY IRRADIATION METHODS IN MICELLAR SYSTEMS

SILBER Rostislav¹, WANGLE Tadeáš¹, ZDYCHOVÁ Vlasta¹

¹Czech Technical University in Prague, Czech Republic, EU
Silber@fffi.cvut.cz

Abstract

This work deals with the preparation of silver nanoparticles using ionizing radiation. The nanosilver was prepared from aqueous solutions of silver nitrate with either Triton X-100 or Brij L4 as the stabilizer and reducing ·OH radical scavenger. The effects of AgNO₃ concentration, dose and type of deposited energy - accelerated electrons, gamma rays or UV - were studied. UV-Vis spectrometry was used to determine the concentration of silver nanoparticles. Photon Cross-correlation Spectroscopy was used to determine particle size in dispersions.

Keywords: Nanosilver preparation, electron, gamma, UV irradiation, micelles

1. INTRODUCTION

Nanoparticles have properties which differ from those of larger particles of the same substance as effects related to surface particles increase in significance. In recent years, many methods have been developed to prepare particles with specific sizes, morphologies and composition. Metal nanoparticles in particular are prized for their many and varied applications. Nanosilver, both pure and in bimetallic particles, has a very wide range of applications. It is well known for its antimicrobial and antifungal properties [1, 2]. Its uses are not, however, limited to those applications and surface-enhanced Raman scattering [3, 4], catalysis [5] are among the other applications worth mentioning. The preparation of nanoparticles of silver using ionizing radiation on solutions of AgNO₃ and nonionic surfactants has the advantages of ionizing radiation, most notably a well regulated reducing or oxidizing environment. Yet it also avoids the downsides: the nonionic surfactants also act as scavengers and subsequent reducing agents, thus eliminating the need to introduce further compounds into the solution.

The goal of this work is to describe the various ways studied - notably electron beam, gamma radiation and UV photolysis - in which nanosilver can be generated from solutions of AgNO₃ in either Triton X-100 or Brij L4 and to describe some of the physicochemical properties of some of the particles prepared. The most notable of these properties are the effects of the initial concentration of AgNO₃ and of the surfactant used on the subsequent concentration of nanoparticles prepared.

The wide variety of reducing methods means that condensing, specifically reducing, methods are the most widely studied. Chemical reduction can rely on strong reducing agents such as NaBH₄ [6] or weaker organic reducing agents, such as L-ascorbic acid [7] or trisodium citrate [8]. Green chemistry - the use of only chemicals not harmful to the environment - has affected the preparation of silver nanoparticles as well.

2. RADIOLYTIC PREPARATION METHODS

During radiolysis of water conventional species such as H⁺, OH⁻ and H₂O₂, as well as several species more reactive than regular chemical compounds, form [9], shown in equation 1. Species thus formed from water compose a majority of the products of ionizing radiation in solutions with concentrations of no more than 1 - 10 wt%.



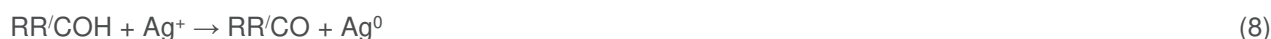
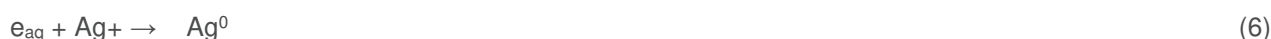
For the reduction of silver ions several of these products are useful. Perhaps the best reducing agent due to its high standard redox potential is the hydrated electron (e_{aq}^-) with $E^0(e_{aq}^-/e^-) = -2.9$ V. These solvated electrons are thermalized and surrounded by oriented water molecules and are highly reactive. A second, weaker reducing agent - which gains significance with decreasing pH values - is the H^\cdot radical which forms according to the reaction in equation 2. It has a standard redox potential $E^0(H^\cdot/H^+)$ of -2.3 V.



The third highly reactive product is the hydroxyl radical $^\cdot OH$, which is a strong oxidizing agent. To be able to produce a reducing environment, the existence of $^\cdot OH$ radicals must be circumvented. To do this, a radical scavenger is chosen to transform the oxidizing $^\cdot OH$ radicals into reducing - if weak - radicals of the scavenger. The general scavenging equation is equation 3. Common scavengers include alcohols (equation 4), such as methanol, ethanol and propan-2-ol and format (equation 5).



Afterwards, the various solvated electrons or reducing radicals act to reduce the silver.



Use ionizing radiation to induce redox reactions has the advantage of a simple relation between the various characteristics of the irradiation and those of the produced nanoparticle. Changes in the dose rate can modify the size; changes in the dose up to a certain level (presumably the reduction of all ions in the solution) increase the concentration [10, 11].

3. STABILIZERS

The high surface energy of silver nanoparticles, which opens up so many new applications, also causes them to be unstable and have a tendency to form aggregates (see equation 6-8). To prevent aggregation, nanosilver must be stabilized in some way. Common methods include dispersing the particles in a gel [69] or adding a stabilizing substance which binds to the molecule. Examples of such substances include polyvinyl pyrrolidone [7], pyridinium di-n-hexaoctyldithiophosphate [8] or substances with -SH groups [9]. A simple separation and stabilization method which relies on physical rather than chemical bonds is the use of surface active substances, which stabilize the silver within micelles.

Nonionic surfactants generally consist of a long polyoxide-ether chain, most commonly a polyethylene glycol ether with an aliphatic and/or aromatic tail. The two surfactants used for the experiments described in this paper were Triton X-100 and Brij L4 (also known under another trade name as Brij 30).

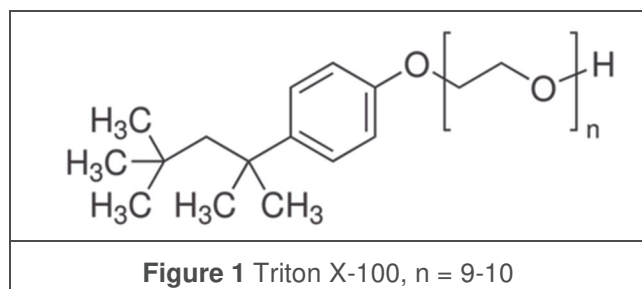


Figure 1 Triton X-100, n = 9-10

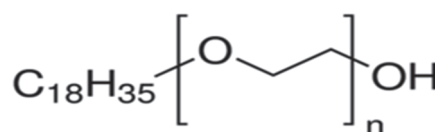


Figure 2 Brij L4, n = 4

Triton X-100 is one of the trade names for 4-(1,1,3,3-Tetramethylbutyl)phenylpolyethylene glycol (see **Figure 2**), where the number of ethylene glycol groups averages between 9 and 10. In an aqueous solution with a pH of less than 8, it takes on the form of a symmetrical 95 700 u particle with a radius of gyration of 2.93 nm. Its critical micellar concentration is 0.2 - 0.9 mmol/dm³ [12], which, given its average molecular weight of 625 g.mol⁻¹, is equal to about 0.013 ± 0.056 w%. Brij L4 is the trade name used to refer to Tetraethylene glycol dodecyl ether [80] (see **Figure 3**). In aqueous solutions it is considerably less soluble than Triton X-100, due to its shorter ethylene glycol chain and is thus prone to forming emulsions rather than colloids. Its critical micellar concentration is about 10 mg/dm³ [13].

Nonionic polyethylene glycol type surfactants were chosen not only for their suitable stabilizing character, but also for their radiation properties. They can act as radical scavengers, forming water and a radical on the first carbon (see equation 9) much like the diols described by Billany et al. [14]. The radical is then free to reduce silver ions in solution or adsorbed on the surface of a silver nanoparticle ($n = 1$, respectively $n > 1$ in equation 10). These reactions are analogous to the reaction with glycol by Soroushian et al. [15].



Where $\text{R} = \text{C}_{12}\text{H}_{25}-(\text{OCH}_2\text{CH}_2)_3$ for Brij or $t\text{-Oct-C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_x$ and $x = 8 - 9$ for Triton X-100.

4. EXPERIMENTAL

4.1. Chemicals

Triton X-100 and AgNO₃ were purchased from Merck. Brij L4 was purchased from Sigma-Aldrich. All chemicals purchased were analytical grade and were used without further purification.

4.2. Sample Preparation

An aqueous solution of the desired surfactant was prepared at the desired concentration (1% for Brij L4 and 2% for Triton X-100) by adding the liquid surfactant to water and continuously mixing it until a homogenous emulsion was formed, in the case of Brij L4, or until the gel formed in the solution was dissolved, in the case of Triton X-100. It usually took about one hour to prepare the desired solution or emulsion. Solid AgNO₃ was then dissolved in the continuously stirred solution (emulsion) and modified by adding small amounts (up to 1 vol%) of a solution of modifier ions. Samples were stored the dark to shield them from the effects of UV light present in natural sunlight.

4.3. Irradiation

Electron Irradiation. A 10 mL sample of the prepared solution was then transferred into 10 or 20 mL ampoules, which were secured with parafilm. The ampoules were placed on a tray on the conveyor and irradiated with 4.5 MeV electrons from a linear accelerator with doses ranging from 1-32 kGy. The samples were placed on the tray all at once and irradiated until a sample was to be taken then irradiation resumed. If the jump between doses increased, then the dose rate was adjusted accordingly. An identical sample containing all the components except the silver nitrate was also irradiated at 24 kGy. This was then used as the standard for taking base readings. This standard was chosen over an unirradiated sample because the quick effects of any UV radiation which, though not significant enough for concentration measurements in UV-Vis spectrometry, play havoc with results from photon cross-correlation spectroscopy, where a very wide range of concentrations is detectable and it is more difficult to establish a good baseline. The other advantage being the possibility to, at least partially, control for chemical changes undergone during radiolysis.

UV Irradiation. A 2 L solution was prepared and then transferred into a 2.8 L glass reactor with three necks. A mercury-vapor medium-pressure lamp was submerged into the solution and the output on the power source was set to 180 increments - roughly equivalent to an output of 400 W.

Gamma Rays. Samples prepared for gamma irradiation were also taken into ampoules just as those for electron irradiation were. The samples were then placed into a 60Co gamma radiation source.

4.4. Instrumentation and Sample Evaluation

UV-Vis Spectrometry. Absorbance at certain peaks serves to describe the concentration of individual species of silver nanoparticles, whereby peaks further in the UV range point to smaller particles. Measurements were performed on a Genesys 20 spectrometer from Thermo Scientific. This spectrometer uses a tungsten and a halogen lamp. The spectrometer can measure in the range of 325–1100 nm. Data was gathered in the VISIONlite control program for the spectrometer. Measurements in that reach further into UV range were performed on a Cary 100 Conc double beam spectrometer from Varian, Inc. This spectrometer was used for measurements in the 190 - 900 nm range. It uses a tungsten halogen lamp for visible light and a deuterium arc as the ultraviolet source and signals are captured on a R928 photomultiplier tube. Analysis was done in the Cary WinUV control program. Samples were measured in plastic cuvettes, except for chloroform solutions, for which fused silica cuvettes were used. Solutions were diluted with water to the concentration necessary to give an absorption in the 0 - 1 range, where the Beer-Lambert law is valid. Standards were used at the same dilution

Photon Cross-correlation Spectroscopy. (PCCS) in the configuration supplied by Sympatec - their NANOPHOX machine in combination with the WINDOX 5 software were used in the measurements described - remains primarily an extension of photon correlation spectroscopy (PCS). The NANOPHOX system uses a He-Ne laser with a wavelength of 632.8 nm with an adjustable position. Samples are kept in a thermostatic bath in photon correlation spectroscopy the scattering of a beam of light on a particle is measured. Such scattering is used to detect the Brownian motion of particles which depends on temperature, the size and shape of the particle, as well as on other factors such as viscosity.

5. RESULTS AND DISCUSSION

5.1. Electron Irradiation

UV-VIS Spectrometry Samples prepared from various concentrations of silver nitrate in a 1 wt% solution of Brij L4 were radiated at doses of 1, 2, 4, 6, 8, 16, 24, 32 kGy. The absorbance of samples was measured from usually to a factor of 1:25 or 1:50, though samples with the highest dose and concentration were diluted up to 1:70. Thus, any absorbances listed are relative to the dilution. The two dependencies studied were the effects of dose and the effects of AgNO₃ concentration on the concentration of Ag nanoparticles. As is visible from **Figures 3** dose causes an almost linear increase in concentration. Concentration as a function of dose only displays a decrease in slope at the highest doses, possibly approaching a plateau. When the initial concentration of AgNO₃ changes, the effects of the dose show similar responses 325 nm to 600 nm with steps

Photon Cross-correlation Spectroscopy Samples prepared from a 0.01 mol/L AgNO₃ solution in both Brij L4 and Triton X-100 were measured by PCCS. The samples in **Figures 4** and **5** show very different of 1 nm. Samples were diluted to put absorbance in the range of 0 - 1 intensities for several peaks. These differences are likely due to the almost double amount of silver nanoparticles formed in the Brij L4 solution by the double dose. Additionally, there are more surfactant molecules in the 2% Triton X-100 solution than in the 1% Brij L4 solution and the Triton X-100 molecules form smaller micelles. One peak is in the single nanometer range, which could belong to the fraction of 2 nm or smaller particles reported by Remita et al. [11]. Most likely, however, they belong to micelles formed by the surfactant. Triton X-100 certainly has a radius of gyration in this range. The second peak is in the 50 - 100 nm range, where the silver nanoparticles are likely to be. This

peak shows considerably smaller particle form in Triton X-100 than in Brij L4. The third peak occurs around 500 nm, this may have formed by coalescing of silver nanoparticles or may be due to dust from the construction taking place near the laboratory in which measurement took place.

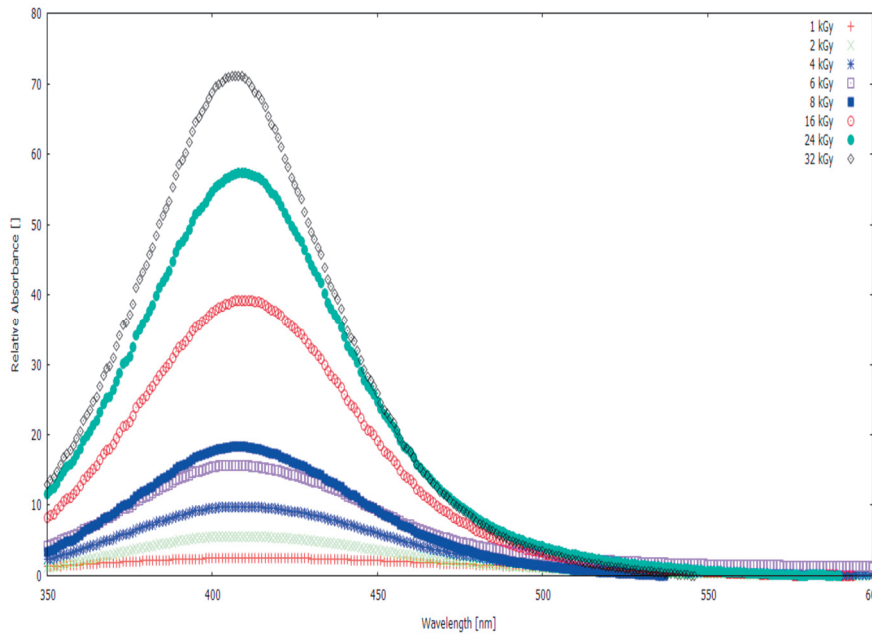


Figure 3 Normalized absorbance spectra for a 0.1 mol/L AgNO₃ sample irradiated with various doses

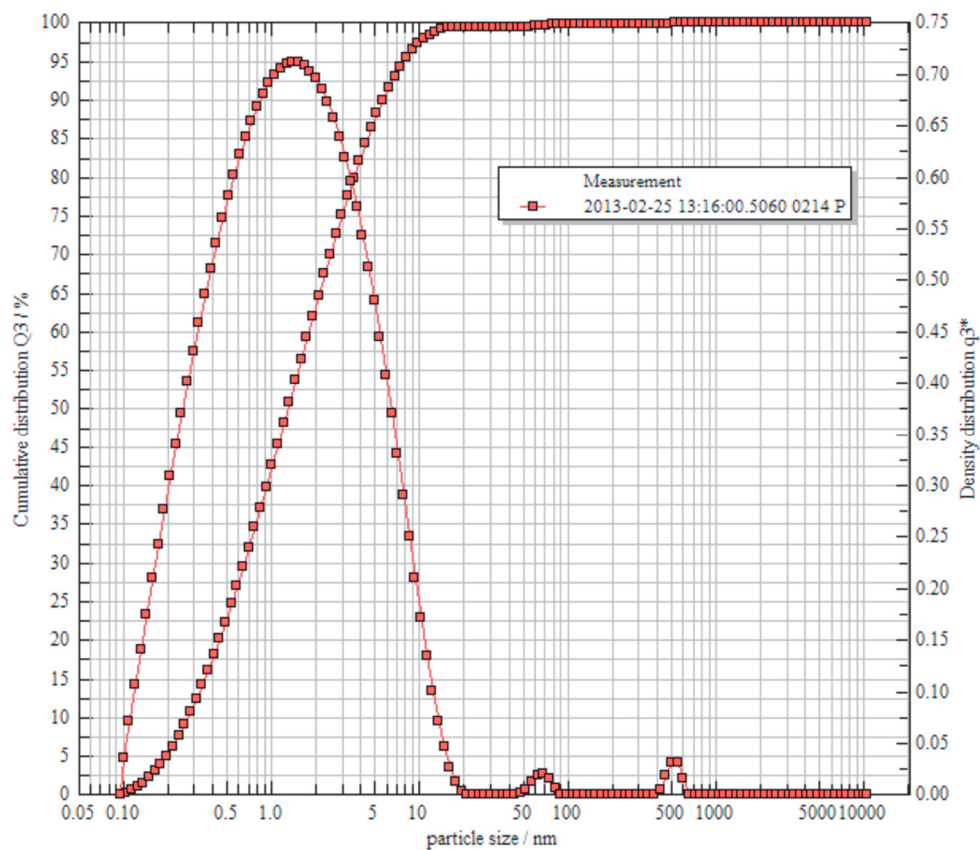


Figure 4 Size distribution for 0.01 mol/L AgNO₃ in Brij L4 irradiated at 24 kGy

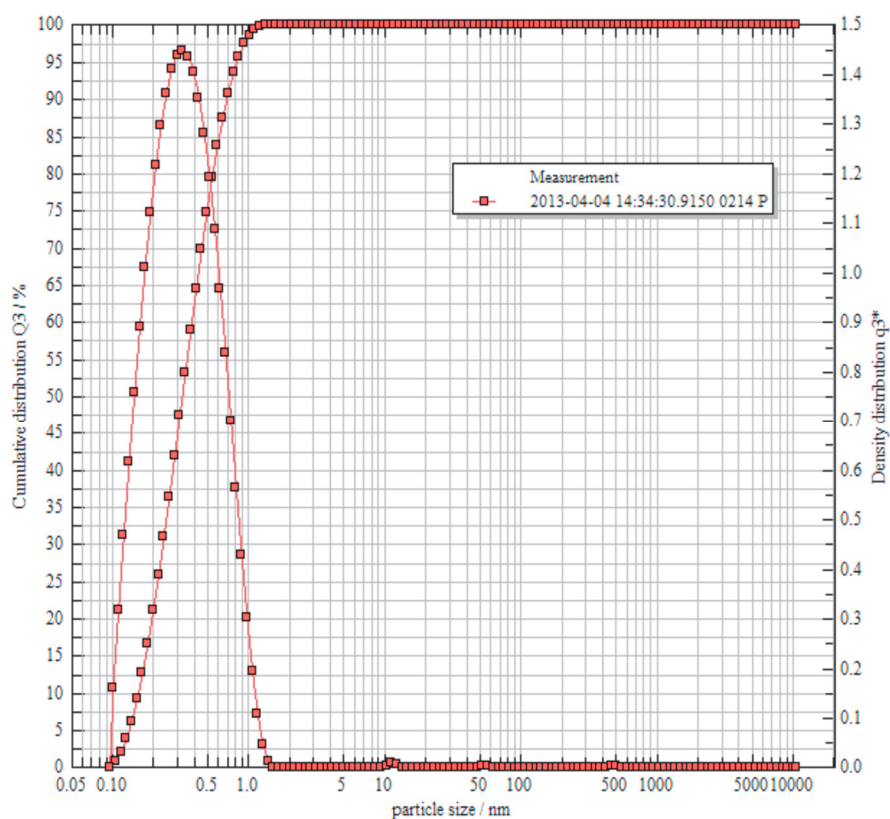


Figure 5 Size distribution for 0.01 mol/L AgNO₃ in Triton X-100 irradiated at 12 kGy

5.2. UV Photolysis

Only one sample was prepared in this way. Though samples were taken at regular intervals from the reactor a tube attached to a syringe, they proved too large to display any of the surface plasmon resonance. The samples were thus impossible to analyze by UV-Vis spectrometry

5.3. Irradiation with Gamma Rays

The dose rate of the ⁶⁰Co source was determined using a Fricke dosimeter. The decrease in dose rate over the period of three months during which samples were prepared was less than 5%, assuming an exponential decrease with the same characteristics as the decay itself. As the measurements are highly sensitive to geometry, that decrease is well within the error margin of the measurement and the dose rate can be assumed to be constant during irradiation. The dose rate was measured to be 55 Gy/h. The concentration of silver nanoparticles in suspension at any one time was affected by two competing factors: the formation of silver nanoparticles by reduction from ions and the sedimentation of formed particles. Despite a decreased need for dilution, samples were diluted to a strength of 1:25 because Brij L4 was tested and known to form a colloid at this concentration instead of the emulsions formed at higher ones. As is visible from **Figure 6**, due to its low dose rate, sedimentation remains the primary determinant of concentration, keeping it constant over a very long period of time. There are two possible factors which may serve as possible explanations for the gradual narrowing of the peak. The first is that initially larger particles form, which would be consistent with the suspension of visible grey microparticles without measurable nanoparticles formed in the sample taken after 24 hours. These larger particles gradually become smaller with increasing dose (an effect reported by Naghavi et al. [10]). The second effect may then be the faster sedimentation of larger particles. Whatever the effects which cause it, the concentration of nanosilver in suspension remains constant over a very long period of time.

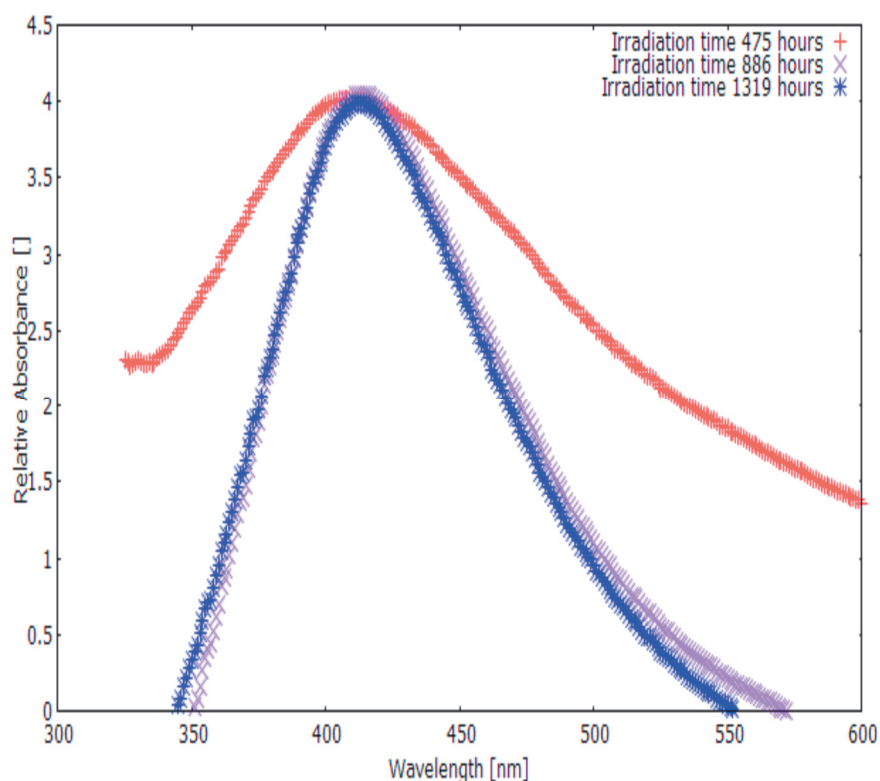


Figure 6 Absorption spectra for a 0.01 mol/L AgNO₃ solution irradiated with gamma rays

6. CONCLUSION

Silver nanoparticles and microparticles were prepared using several different ionizing particles: accelerated electrons and UV and gamma photons. For accelerated electrons, it was confirmed using UV-Vis spectrometry that an increase in the dose leads to a larger concentration of silver nanoparticles. It was also found that an increase in the initial concentration of silver nitrate will generate more nanoparticles. Every concentration responds in a similar, linear manner to an increase in dose. The slopes of the linear responses increase with the concentration, though that increase seems to be approaching a plateau. Using photon cross-correlation spectroscopy, it was confirmed that 50-100 nm particles are produced and that smaller particles form in Triton X-100 than in Brij L4. For UV photons microparticles were prepared in Brij L4. For gamma rays with a low dose rate, it was confirmed using UV-Vis spectrometry that an equilibrium of sorts forms between the production and sedimentation of silver nanoparticles. From the shape of the spectra, it can be surmised that the particles in the solution gradually decrease in size until they reach a constant value.

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