PLASMA-CHEMICAL FORMATION OF SILVER NANOPARTICLES: THE SILVER IONS CONCENTRATION EFFECT ON THE PARTICLE SIZE AND THEIR ANTIMICROBIAL PROPERTIES

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ABSTRACT

Silver nanoparticles (AgNPs) are prepared by plasma-chemical discharge irradiation of silver nitrate solution without using reducing or capping agents. The nanoparticles are characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and ultraviolet–visible (UV–Vis) absorption spectroscopy. The effect of the silver ions concentration on the size of the silver particles is studied. The optical absorption spectroscopy of AgNPs prepared at different silver ions concentrations shows a surface plasmon resonance at ca 395 nm - 440 nm. Spherical, nanometer-sized particles are obtained. The average particle size is observed to increase with the initial AgNO_3 concentration increase. Highly monodispersed silver nanoparticles are obtained within 5 min of plasma irradiation. XRD analysis reveals that the particles are face-centred cubic one. The synthesized silver nanoparticles have a significant antibacterial activity on two strains of Gram bacteria.

Keywords: silver nanoparticles, ions concentrations, average diameters, antibacterial activity.

INTRODUCTION

The area of nanoparticles research has witnessed tremendous growth due to the unusual chemical and physical properties demonstrated by this intermediate state of matter [1]. Due to their small size, these crystallites exhibit novel material properties that largely differ from those of the bulk [1]. Silver nanoparticles (AgNPs) represent one of the most extensively studied nanomaterials, which fascinate scientists due to their promising practical applications [2]. In the United States, more than $4 \cdot 10^6$ tons of silver have been consumed in 2000. Hence, synthesis strategies that result in controlled NP size, distribution, shape and stability are still an area of interest.

One of the innovative and environmentally safe methods for preparation of nanosized compounds is the use of plasma discharges of various configurations: plasma discharge generated between electrodes immersed in the liquid, at gas-liquid phase interface at reduced pressure, plasma at atmospheric pressure in an interaction with a liquid [3 - 6].

Among plasma-chemical discharges, contact non-equilibrium low-temperature plasma (CNP) is a promising option from the point of view of practical application [7]. It is generated between an electrode in the gaseous phase and another one located at the surface of a liquid. Therefore, the chemical transformations at the interface considered are conditioned by the combined effect of an electrochemical oxidation-reduction, an initiated

photolysis reaction, UV radiation, and a flow of charged particles from the gaseous phase to the surface of the liquid medium. By varying the liquid phases' composition it is possible, to a certain degree, to manage the paths of the chemical transformations and the composition of the products obtained [7]. In their previous works the authors have shown the efficiency of using contact non-equilibrium low-temperature plasma in comparison with the conventional method of chemical reduction in solutions and photochemical deposition [8]. The efficiency of CNP use for fabrication of silver nanoparticles from aqueous solutions of metal salts in presence of sodium alginate [9], citrate [10], and polyvinyl alcohol [11] is demonstrated. The thermodynamics and kinetics analysis of the plasmochemical formation of AgNPs is treated elsewhere [12]. It is well known that the parameters of AgNPs (morphology, size distribution, etc.) depend on the reaction conditions (the precursor concentration, the metallic salt/reducing agent molar ratio, etc.).

The present study is designed to identify the effects of variation of the composition of the liquid phase (of the silver ions initial concentration) on plasma-chemical obtaining of colloidal solutions of silver nanoparticles and their parameters.

EXPERIMENTAL
Materials

Silver nitrate (99.8 %, Kishida) was purchased from Merck Co. Ltd. (Darmstadt, Germany). The aqueous solutions of silver nitrate of a different concentration were prepared using ultrapure water (Direct-Q UV, Millipore) and were utilized as starting materials without further purification.

Equipment

The research was carried out at the laboratory of plasma-chemical technologies of the Ukrainian State Chemical Technology University (Ukraine) on a laboratory installation of a discrete type with a reactor volume of 0.1 ml [8 - 12]. The cathode (of a diameter of 4 mm made of 18H10T stainless steel) was located in the liquid phase, while the anode (of a diameter of 2.4 mm) was placed at the distance of 10 mm from the solution surface. The volume of the solution in the reactor was

equal to 70 ml. The cooling of the reaction mixture was provided by continuous circulation of cold water. The pressure in the reactor was maintained at 80±4 kPa. For obtaining plasma discharge the voltage of 500 V - 1000 V was applied to the electrodes. The current strength was maintained at the level of 120±6 mA. The duration of the plasma processing of the solutions was equal to 5 min.

Characterization techniques

The spectrum of the colloidal solutions was obtained by spectrophotometer UV-5800PC using quartz cuvettes in the wavelength range of 190 nm - 700 nm (FRU, China).

The particle size in the colloidal solutions was measured by Zetasizer Nano-25 (Malvern Instruments Ltd., Malvern, England).

The disperse phase of the solution was obtained as a result of the plasma-chemical treatment of the solution and dried in the air at 25°C. It was studied with X-ray diffractometer Ultima IV Rigaku. In addition, the presence of metals in the sample was identified by energy dispersive spectroscopy (EDS).

A drop of the plasma synthesized AgNPs dispersion was placed on a carbon-coated copper grid and dried at room temperature. A TEM micrograph of the sample was taken using JEOL TEM (Model 100 CX II; Tokyo, Japan). The size and the shape of AgNPs were studied.

Preparation of silver nanoparticles AgNPs

In order to synthesize surfactant-free AgNPs, an atmospheric CNP was generated at the surface of a silver nitrate aqueous solution (of $AgNO_3$ concentration of 0.25 mmol/L - 3.0 mmol/L). The silver nitrate aqueous solution was treated in the reactor with the discharge of contact non-equilibrium low-temperature plasma of fixed parameters (time, pressure, current strength). The plasma parameters were as follows - the duration of the solutions plasma processing was equal to 5 min, the current strength was maintained at 120±6 mA, the pressure in the reactor was maintained at 80±4 kPa. The interactions of the gas-phase plasma with the solution initiated liquid-based reactions that determined the nucleation and growth of AgNPs on the ground of the silver precursor ($AgNO_3$) reduction. The plasma-liquid
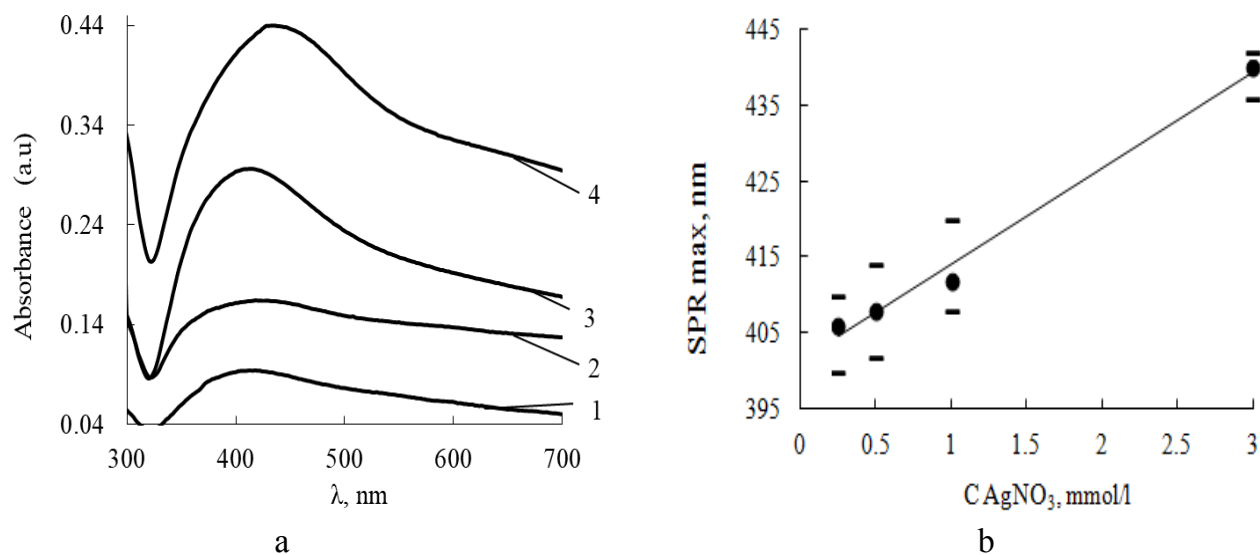
Fig. 1. a) UV-Visible spectra and b) surface plasmon resonance (SPR) of silver nanoparticles obtained by plasma discharge at a different concentration of $AgNO_3$, (mmol/L): 1 - 0.25; 2 - 0.5; 3 - 1.0; 4 - 3.0.

interface was possibly represented by a gas/water vapour plasma environment where the electrons were believed to be responsible for initiating the reactions in the liquid solution which subsequently cascaded. The final product was obtained as a colloidal dispersion. The samples were analyzed by UV-Vis immediately after preparation.

Assay for antimicrobial activity of Ag nanoparticles against microorganisms

The disk diffusion method was used to study the antibacterial activity of the synthesized silver nanoparticles. *Staphylococcus aureus* and *Escherichia coli* were used as model test strains for Gram-positive and Gram-negative bacteria, respectively. The bacterial suspension (About 10^4 colony forming units (CFUs) of freshly cultured microbial cells) was spread on nutrient agar in a Petri plate to create confluent lawn of bacterial growth. The wells of 5 mm were prepared by a borer. The solutions of different AgNPs concentrations (15 μL) were poured into each well. The well without silver nanoparticles was treated as a control (water) sample. After 24 h of incubation at 37°C, the dimensions of the inhibition zones around the samples were measured in five directions, and the average values were used to calculate the circle zone area.

RESULTS AND DISCUSSION

The synthesis of AgNPs is compared by varying the silver precursor concentration while keeping constant the processing current at 120 mA. According to the Mi-Droude theory, the optical properties of the colloidal solutions of nanoparticles of metals are characterized by the presence of a pronounced resonant absorption spectrum of the surface plasmon resonance (SPR) in the visible spectrum. The positions of the maximum SPP serve as a characteristic of both the form of the existence of colloidal silver in the aqueous medium and the size of the nanoparticles [13]. It is well recognized that the maximum absorption of silver nanoparticles of a spherical shape is characterized by the presence of a maximum absorption in the range of 350 nm - 440 nm [13].

Fig. 1 shows the UV-Vis spectrum and the surface plasmon resonance (SPR) of colloidal silver nanoparticles prepared by the plasma-chemical method with different initial $AgNO_3$ concentrations.

The data reveals a number of findings which can be presented as follows: (i) the initial molar concentration of the precursor affects the absorption resonant peak wavelength of the plasma-processed solution. The absorption peak at ca 400 nm - 440 nm in Fig. 1(a) is

Table 1. An average size of silver nanoparticles prepared by plasma discharge method.

C AgNO$_3$, mmol/L	Average size AgNPs, nm
0.25	36.5±1.2
0.5	38.0±2.3
1.0	50.1±2.7
3.0	60.1±2.0

attributed to the surface plasmon excitation of silver lone spherical or roughly spherical Ag nanoparticles [14]; (ii) the intensity of the maximum plasmon peak increases with increase of the AgNO$_3$ concentration indicating that a higher concentrations of silver nanoparticles are formed. At the same time, an increase of the peak of surface plasmon resonance is observed Fig. 1(b) with increase of the precursor's concentration. This indicates that the size of the silver particles that are formed is increasing [15]. This suggests in particular that the precursor concentration could be used to control the size of the synthesized NPs.

The size of the particles formed in the aqueous solution under plasma discharge conditions is determined. To do this, a study of particle size distribution is performed, and the average particle size (Table 1) of plasmochemically prepared silver dispersions at different initial concentrations of Ag$^+$ is determined. As a result of the plasmochemical impact, silver nanoparticles of a wide size distribution are formed. The data obtained (Table 1) indicates that the average diameter of the nanoparticles formed under plasma discharge impact is 36.5 nm - 60.1 nm and increases with increase of the initial concentration of Ag$^+$.
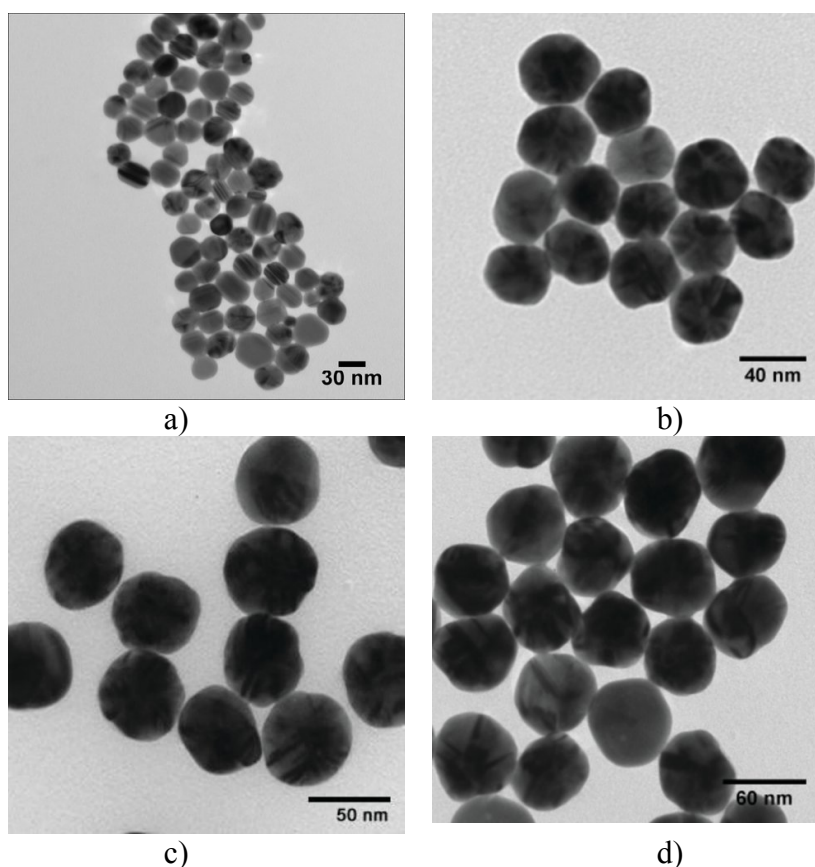

a)

b)

c)

d)

Fig. 2. TEM-image of plasma discharge obtained nanoparticles of silver at a different concentration of AgNO$_3$, mmol/L: 0.25 (a), 0.5 (b), 1.0 (c), 3.0 (d).

TEM analysis is also used to determine the particle shape distribution and the morphology for the same set of four processing conditions (AgNO$_3$ concentration of 0.25 mmol/L - 3.0 mmol/L; a discharge current of 120 mA).

A typical TEM image of Ag nanoparticles obtained at a different concentration of AgNO$_3$ is shown in Fig. 2. Spherical particles of 30 nm - 60 nm diameter are seen. They are also found to be highly monodispersed and uniformly distributed. At all molar concentrations the synthesized particles of silver are spherical. The average size of the silver particles increases with increase of AgNO$_3$ concentration.
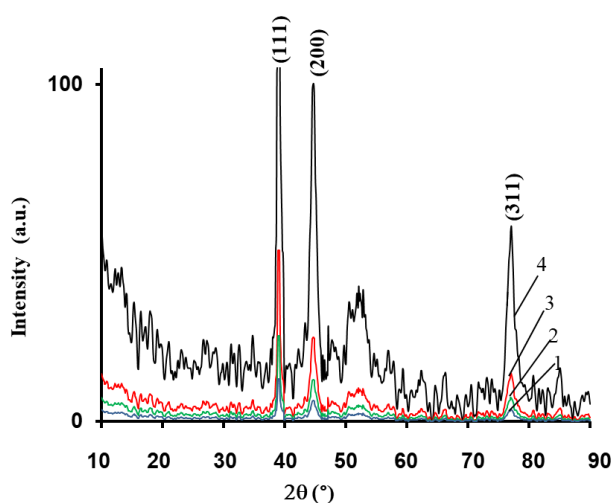

Fig. 3. An X-ray diffraction pattern of silver nanoparticles prepared by discharge plasma at a different concentration of AgNO$_3$, mmol/L: 0.25 (a), 0.5 (b), 1.0 (c), 3.0 (d).
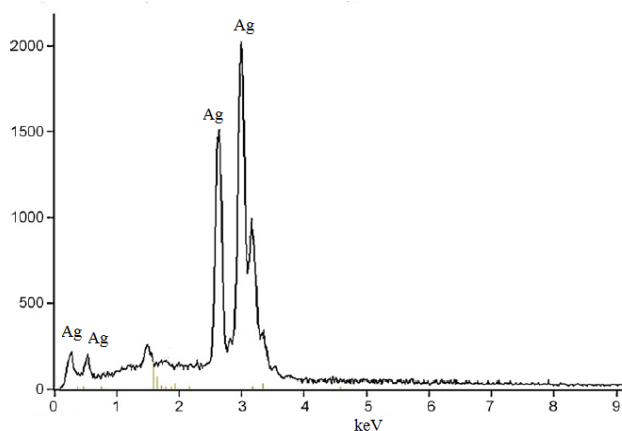

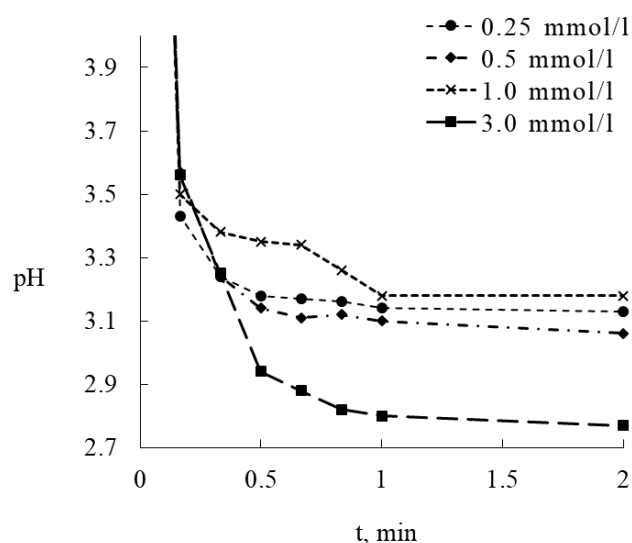Fig. 4. EDS analysis of silver nanoparticles prepared by discharge plasma.

Fig. 5. A change of AgNO$_3$ aqueous solution pH as a function of the discharge duration at a different concentration of AgNO$_3$, mmol/l: 0.25 (1), 0.5 (2), 1.0 (3), 3.0 (4).

The formation of metal silver is confirmed by powder X-ray diffraction (XRD) analysis. The conditions of the experiment are as follows: I = 120 mA, P = 0.08 MPa, τ = 5 min, C$_{AgNO3}$ = 0.25 mmol/L - 3.0 mmol/L.
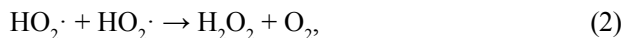
Fig. 3 shows a typical XRD pattern of silver nanoparticles obtained in all samples: peaks at 2θ values of 38.1 deg, 44.9 deg, 77.5 deg can be attributed to the (111), (200), (311) crystalline planes of the face centered cubic crystalline structure of metallic silver. The intensity of the peaks reflects the high degree of crystallinity of the silver nanoparticles [15]. The EDS spectrum (Fig. 4) recorded of silver nanoparticles shows a strong signal of silver (the conditions of experiment are as follows: I = 120 mA, P = 0.08 MPa, τ = 5 min; C$_{AgNO3}$ = 3.0 mmol/L).

Fig. 5 shows the change of AgNO$_3$ aqueous solution pH as a function of the discharge duration. It is evident that the solution pH decreases steadily during the treatment from 7.0 - 7.27 to 2.6 - 2.9 at different concentrations of silver ions. The intense decrease of the solution acidity is likely to be due to the consumption of OH radicals in hydrogen polyoxides formation and the transfer of electrons of H radicals to the solution. After the rapid decrease of pH to 3.4 - 3.7, the pH value is stabilized and kept constant.

The previous publications of the authors [8] have shown that atomic hydrogen, atomic oxygen, and hydroxyl radicals are generated in the course of the

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processes at the liquid–gas interface induced by contact nonequilibrium plasma and expressed in terms of the classical scheme adopted for chain reactions.

The formation of hydrogen peroxide as a final product can also be ranged as a chain termination step:

$$\cdot OH + \cdot OH \rightarrow H_2O_2, \tag{1}$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2, \tag{2}$$
$$HO_2\cdot + \cdot H \rightarrow H_2O_2 \tag{3}$$

The hydrogen peroxide accumulating in the course of the chemical transformations tends to polymerize to form hydrogen polyoxides. In general, the process can be described by the following overall equation:

$$(n-1)H_2O_2 \rightarrow HO_nH + (n-2)H_2O.$$
$$(\Delta G_0, -122.83 \text{ to } -596.93 \text{ kJ/mol}) \tag{4}$$
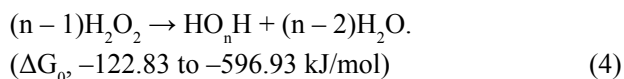
The OH radicals produce hydrogen peroxide (H_2O_2), while the hydrogen radicals are used to generate Ag nanoparticles in the reduction process. The role of the hydrogen radicals in plasma synthesis of metal nanoparticles in a solution is suggested based on the electron spin resonance spectroscopic (ESR) measurements [15].

Upon the irradiation of electrons from CNP discharge, a considerable number of hydrated electrons is generated near the plasma–liquid [8, 16]. Then, the hydrated electrons reduce Ag^+ to Ag^0

$$Ag^+ + e_{aq-} \rightarrow Ag, \text{ k=3.3} \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1} \tag{5}$$
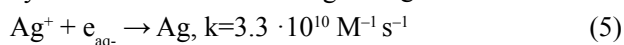
which contributes to the formation of Ag nanoparticles nuclei. This reaction has a fast rate constant [15]; thus, the generation of Ag nanoparticles by electron irradiation from plasma is reasonable. H radicals may also reduce Ag^+, where the H radicals are obtained from the dissociation of H_2O.

$$Ag^+ + H^- \rightarrow Ag + H^+, \text{ k=2.2} \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1} \tag{6}$$
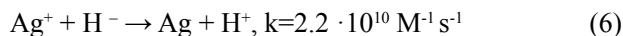
This reaction has also a high rate constant [16]. The authors suggest that the dominant reducing agent in the synthesis of Ag nanoparticles is the H radical, which is effectively generated by high-energy positive ions accelerated in the cathode fall region via the dissociation of liquid molecules in a low pressure CNP discharge in contact with the liquid.

Silver nanoparticles are known for their antimicrobial properties and have been used for years for antimicrobial applications [16, 17]. Additionally, silver has been used in water and air filtration to eliminate microorganisms. The antimicrobial activity of the plasma synthesized Ag NPs is examined by the well diffusion method. The diameter of the inhibition zones (in millimeters) around the different silver nanoparticles sols with a test strain are shown in Table 2.

It is seen that SNPs exhibit a good antibacterial activity against both Gram-negative and Gram-positive bacteria. The zone of inhibition ranges from 3 mm to 28 mm. The control sample (with deionized water) exhibits zero zone of inhibition (ZI). The increase of the silver ions concentration increases the antimicrobial activity. The differential sensitivity of Gram-negative and Gram-positive bacteria toward AgNPs can be attributed to the difference in their cell walls structure. The cell wall of the Gram-positive bacteria is composed of a thick layer of peptidoglycan containing linear polysaccharide chains cross-linked by short peptides. Thus, a more rigid structure is formed which hampers the penetration of the silver nanoparticles. The cell walls of the Gram-positive bacteria have a thinner layer of peptidoglycan [18].

Table 2. Zone of inhibition of synthesized silver nanoparticles against bacterial pathogens.

Test organism	Zone of inhibition (mm)				
	Control Sterilized water (de-ionized)	C AgNO₃, mmol/l			
		0.25	0.5	0.1	0.3
Escherichia coli	0	7	22	25	28
Staphylococcus aureus	0	3	10	20	25

CONCLUSIONS

This study shows that plasma-chemical discharge irradiation provides a fast and eco-friendly method for the synthesis of silver nanoparticles from silver nitrate solution. Spherical, monodispersed silver nanoparticles are synthesized under contact non-equilibrium low-temperature plasma without using reducing or capping agents. The formation of silver colloidal solutions is characterized by the presence of a peak at λ_{max} = 400 - 440 nm in the spectrum. Through transmission electron microscopy silver nanoparticles are observed to be spherical with a diameter of up to 100 nm. The average particle size is found to increase with the initial $AgNO_3$ concentration increase. The formation of silver metal particles is confirmed by X-ray diffraction analysis. This rapid synthesis technique can be a promising method for the preparation of highly monodispersed spherical silver nanoparticles. It can be applied to other noble metals nanoparticles formation.

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