SHAPE AND SIZE CONTROLLED SYNTHESIS OF SILVER NANOPARTICLES UNDER DIFFERENT REACTION CONDTIONS

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Abstract

This paper deals with the synthesis of silver nanoparticles (Ag NPs) under different reaction conditions, such as temperature and UV irradiation. We investigated how these variant parameters can affect the final properties of Ag NPs, mostly their size, shape and stability. It is well known that diameter and shape of nanoparticles influence their physical, biological and chemical properties and thus predict their applications in different fields. Tailoring final features of Ag NPs during the synthesis gives us the possibility to prepare nanoparticles with required properties, specifically as antimicrobial or antifungal agents. The prepared nanoparticles were characterized by following methods; transmission electron microscopy, scanning electron microscopy and absorbance in UV-VIS region.

Keywords: Silver nanoparticles, synthesis, UV irradiation, temperature, shape, size

1. INTRODUCTION

Nowadays, nanochemistry frequently uses metallic nanoparticles with unique properties, compared to their macro scaled counterparts, coming from their high surface to volume ratio [1, 2]. Silver nanoparticles (further denoted as Ag NPs) can be utilized thanks to their remarkably distinct physical, biological and chemical properties in various research areas such as physics, optics, chemistry, biology, pharmacy or medicine [3, 4]. These features of Ag NPs are significantly affected by their shape and size [5, 6]. The ideal Ag NPs should have small particle dimension, high surface area, quantum confinement or colloidal stability [1,2]. Recently Ag NPs have been used for antimicrobial purposes [3]. For instance, antibacterial activity is very favorite not just in research or medicine but also in commercial products such as clothes with nanosilver exploited for instance in army [7]. This antibacterial effect is very closely related with Ag NPs size; general postulate is that the smaller is the silver nuclei, the higher is antibacterial activity [8]. Control of size and shape of Ag NPs can be reached by various preparation techniques using reducing agents and stabilizers. It is also well known that silver based materials are significantly toxic to microorganisms; exactly to 16 major species of bacteria including *E. coli* [9]. However, in many of these applications the Ag NPs are not sufficiently bonded to the surface of material and after few cycles of usage are easily released to the aquatic environment where causing irreversible changes in living organisms [10]. Thus their covalent bonding to the material is very important and challenging, while remaining their antimicrobial features. Therefore, the key step is to provide suitable stabilization coating for Ag NPs together with their effective immobilization on any requested surface.

2. EXPERIMENTAL PART

2.1. Chemicals

Silver nitrate was purchased from PENTA and both reducing agents were purchased from Sigma Aldrich. All materials with chemical purity p.a. were used without further purification. Every reaction reagent was prepared in aqueous solution using demineralized water.

2.2. Synthesis of silver nanoparticles

Ag NPs were prepared by wet chemical method. The synthesis was based on a precursor of silver ions, i.e. 1 mM silver nitrate solution which was reduced by two different reducing agents poured to the reaction solution at the same time. The first reducing agent was 2 mM sodium citrate solution. Sodium citrate is a weak reducing agent, if it would be used as the only reducing agent, it would significantly prolong the time of reaction and its interaction with silver nitrate is happening only at higher temperature, approx. 80 °C [11]. Sodium citrate plays also a role of stabilizer. The second used reducing agent was 1 mM hydrazine hydrate, which is a strong reducing agent. The reaction solution was placed on magnetic stirrer with 200 rpm during entire reaction and time of reaction was 30 min.

Four different temperatures, namely 30 °C, 40 °C, 60 °C, and 80 °C were investigated as a parameter affecting the properties of Ag NPs such as the size and shape. All aqueous solutions were heated to the same desired temperature. This reaction was performed in the dark place.

Another tested parameter during the synthesis was a different wavelength of UV irradiation, namely: 254 nm, 366 nm and 400 nm. These three types of reactions were held at temperature of 22 °C. UV source with radiance intensity of 5 mW/cm^2 was placed in 3 cm above the top of the beaker with reaction solution.

Final colloidal solutions of Ag NPs were purified by ultracentrifugation at 14 500 rpm three times for 30 min. Ag NPs were stored in demineralized water in dark bottle in the fridge. Ag NPs were characterized by several methods to determine their size and shape; scanning electron microscopy (SEM), transmission electron microscopy (TEM) and absorbance in UV-VIS region.

3. RESULTS AND DISCUSSION

We investigated an effect of two synthesis parameters, namely temperature and wavelength of UV irradiation on final properties of Ag NPs. All prepared samples and conditions of experiments are listed in the **Table 1** below.

Table 1 List of prepared samples of Ag NPs under different conditions

sample name	wavelength (nm)	temperature (°C)
Ag 30	darkness	30
Ag 40	darkness	40
Ag 60	darkness	60
Ag 80	darkness	80
Ag 254	254	22
Ag 366	366	22
Ag 400	400	22

3.1. Effect of different temperature

The first investigated parameter was the temperature. According to SEM analysis, the changing temperature significantly affected the Ag NPs shape and size distribution as well. **Figure 1** shows SEM images of all Ag

NPs samples prepared at different reaction temperatures: 30 °C (sample Ag 30), 40 °C (sample Ag 40), 60 °C (sample Ag 60) and 80 °C (sample Ag 80). Color of sample Ag 30 changed immediately after adding reducing solutions into nitrate solution to dark green. Size and also shape distribution is very broad: there is no shape or size population which dominates. Shape of Ag NPs is anisotropic and asymmetric with mostly squared or sharp edges. Ag NPs from sample Ag 40 started to form immediately after adding reducing agents into aqueous solution of silver nitrate, which was observed by changing of color to dark green. These Ag NPs are very similar to previous sample at shape and size distribution but Ag NPs from this sample have more rounded shapes and edges and the amount of Ag NPs with smaller diameter increased as well. Color of sample Ag 60 changed immediately after adding reducing solutions into silver nitrate solution to dark red, which pointed to creation of Ag NPs. Size and shape of Ag NPs are closer to homogeneous distribution than in two previous samples. Shape of these Ag NPs is nearly spherical. Sample Ag 80 changed color to dark red immediately after adding reducing agents into solution of silver nitrate. Ag NPs are separated and covered probably by sodium citrate, which plays a role of stabilization of Ag NPs. Shape is nearly spherical. All prepared solutions were stable for 7 days after preparation; a sediment on the bottom of the vessel was observed after this period.

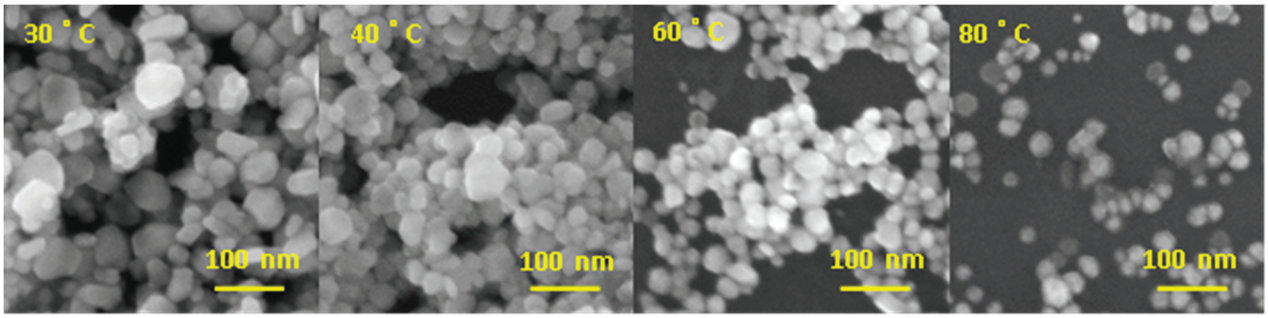

Figure 1 SEM images of Ag NPs prepared at different temperatures: 30 °C, 40 °C, 60 °C, 80 °C

Figure 2 shows absorption spectra of samples Ag 30, Ag 40, Ag 60 and Ag 80 with absorption maximum of surface plasmon resonance (SPR) at 420 nm, which is typical for Ag NPs. It is visible that with increasing temperature, the broadness of absorption peaks decreases, which points to decreasing size of Ag NPs what, is confirmed by SEM analysis as well.

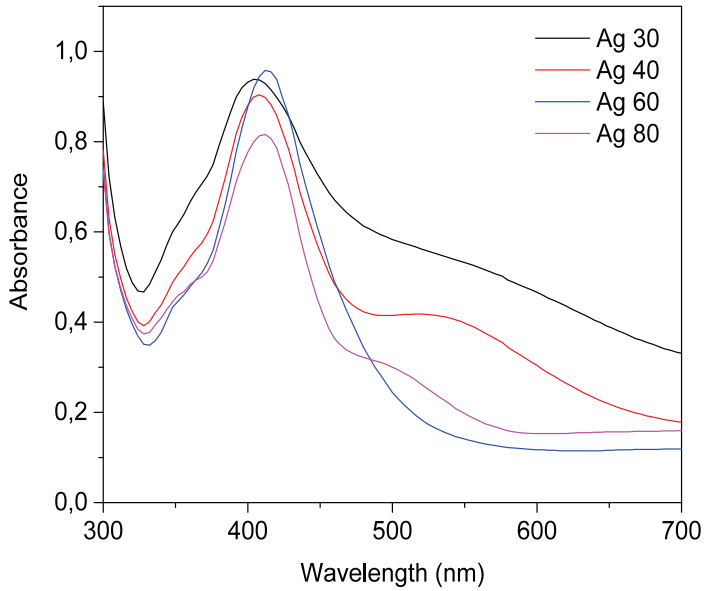

Figure 2 Absorbance spectra of Ag NPs prepared under different temperatures; 30 °C, 40 °C, 60 °C, 80 °C

3.2. Effect of different wavelength

The second investigated parameter was UV irradiation with three different wavelengths - 254 nm, 366 nm and 400 nm. **Figure 3** shows SEM analysis of samples Ag 254, Ag 366 and Ag 400. Color of all solutions turned to green in 1 min after addition of reducing solutions into aqueous solution of silver nitrate. Sample Ag 254 evince Ag NPs with smaller diameter and nearly spherical shape. Sample Ag 366 shows Ag NPs with mostly rounded shape but amount of Ag NPs with bigger diameter increased. Sample Ag 400 shows very broad size and shape distribution; it includes nearly spherical Ag NPs with smaller diameter and also bigger objects with higher diameter and anisotropic shape. According to the literature, with longer wavelengths the shape of Ag NPs should turn from spherical to anisotropic. These colloidal solutions were stable for 5 weeks from preparation procedure [5, 12].

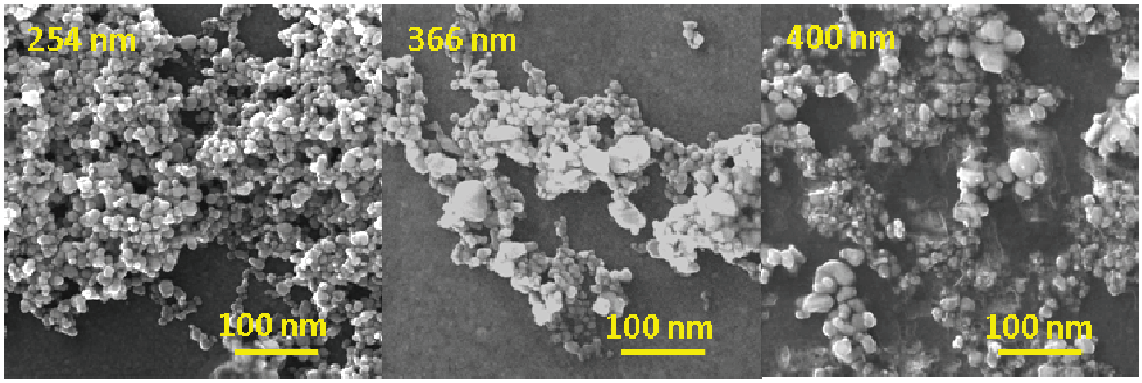

Figure 3 SEM images of Ag NPs prepared under UV irradiation with three different wavelengths: 254 nm, 366 nm and 400 nm

TEM images in **Figure 4** show Ag NPs prepared under UV irradiation with three different wavelengths; 254 nm, 366 nm and 400 nm. Ag NPs from sample Ag 254 evince spherical shape with diameter about 50 nm. Size and shape distribution of Ag NPs in colloidal solution Ag 366 with increasing wavelength changed to broad. This sample includes triangles with truncated tops, spheres and also rods. Ag NPs from sample Ag 400 are very similar to sample Ag 366. Their size and shape distribution is also very broad but amount of Ag NPs with anisotropic shape increased. The mean size of Ag NPs is from 10 nm up to 50 nm.

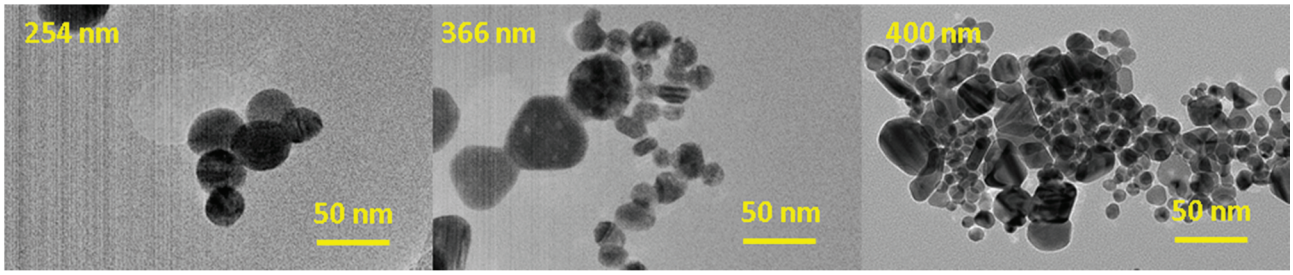

Figure 4 TEM images of Ag NPs prepared under UV irradiation with three different wavelengths; 254 nm, 366 m, and 400 nm

Absorption spectra of samples Ag 254, Ag 366 and Ag 400 are shown in **Figure 5**. All samples have typical absorption maximum of SPR at wavelength of 420 nm. The absorption spectra of samples Ag 254 and Ag 366 are very similar. Absorption spectrum of sample Ag 400 is different; it exhibits the secondary absorption peak at longer wavelengths which is caused by Ag NPs with anisotropic shape [13]. Intensity of absorbance is different at each sample; it is caused by different concentration of Ag NPs in colloidal solution.

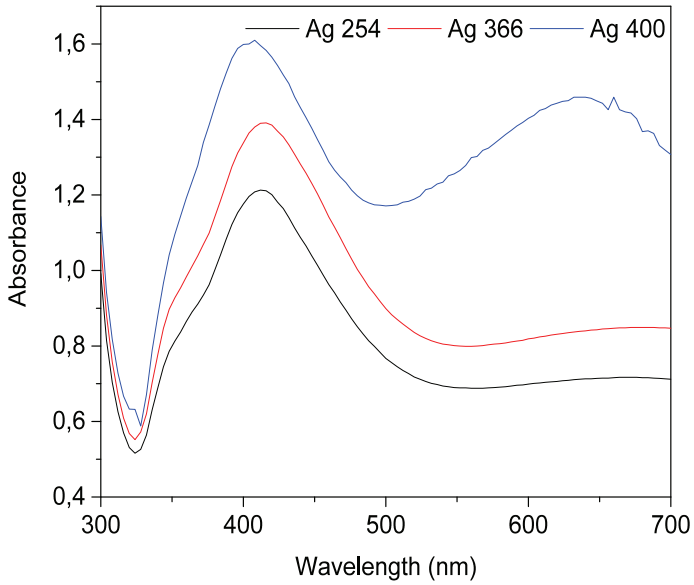

Figure 5 Absorbance spectra of Ag NPs prepared under UV irradiation with three different wavelengths; 254 nm, 366 nm and 400 nm

4. CONCLUSION

It is visible that the changing conditions such as temperature and UV irradiation with different wavelengths can significantly change final Ag NPs in solution; mostly their size and shape. With changing temperature, Ag NPs changed their size and shape. Employing higher temperature resulted in more narrow distribution of Ag NPs, where spherical shape became dominant together with smaller diameter of Ag NPs. UV-induced synthesis seems to be very efficient route how to prepare Ag NPs with exact physical properties for specific application as well. Utilization of different wavelengths can significantly affect size and shape distribution of colloidal Ag NPs. The shorter was the wavelength, the more spherical shape and smaller diameter of Ag NPs were observed. Size or anisotropic shape of Ag NPs can significantly affect absorption spectra of Ag NPs, which can be visible as an occurrence of more peaks in absorption spectrum.

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REFERENCES

[1] GUZMÁN, M. G.; DILLE, J.; GODET, S., Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity. *Int J Chem Biomol Eng* **2009,** 2, (3), 104-111.

[2] TRAN, Q. H.; LE, A.-T., Silver nanoparticles: synthesis, properties, toxicology, applications and perspectives. *Advances in Natural Sciences: Nanoscience and Nanotechnology* **2013,** 4, (3), 033001.

[3] PRABHU, S.; POULOSE, E., Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. *Int Nano Lett* **2012,** 2, (1), 1-10.

[4] PALZA, H., Antimicrobial Polymers with Metal Nanoparticles. *International journal of molecular sciences* **2015,** 16, (1), 2099-2116.

[5] WILEY, B.; SUN, Y.; MAYERS, B.; XIA, Y., Shape-controlled synthesis of metal nanostructures: the case of silver. *Chemistry-A European Journal* **2005,** 11, (2), 454-463.

[6] CALLEGARI, A.; TONTI, D.; CHERGUI, M., Photochemically grown silver nanoparticles with wavelength-controlled size and shape. *Nano Letters* **2003,** 3, (11), 1565-1568.

[7] RAI, M.; YADAV, A.; GADE, A., Silver nanoparticles as a new generation of antimicrobials. *Biotechnology Advances* **2009,** 27, (1), 76-83.

[8] KIM, J. S.; KUK, E.; YU, K. N.; KIM, J.-H.; PARK, S. J.; LEE, H. J.; KIM, S. H.; PARK, Y. K.; PARK, Y. H.; HWANG, C.-Y.; KIM, Y.-K.; LEE, Y.-S.; JEONG, D. H.; CHO, M.-H., Antimicrobial effects of silver nanoparticles (vol 1, pg 95, 2007). *Nanomedicine-Nanotechnology Biology and Medicine* **2014,** 10, (5), 1119-1119.

[9] DAS, R.; GANG, S.; NATH, S. S., Preparation and antibacterial activity of silver nanoparticles. *Journal of Biomaterials and nanobiotechnology* **2011,** 2, 472.

[10] PRABHU, S.; POULOSE, E. K., Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. *Int Nano Lett* **2012,** 2, (1), 32.

[11] GUZMAN, M.; DILLE, J.; GODET, S., *Synthesis and Antibacterial Activity of Silver Nanoparticles Against Gram-Positive and Gram-Negative Bacteria*.Journal? 2011;. 8, p 37-45.

[12] XUE, C.; MÉTRAUX, G. S.; MILLSTONE, J. E.; MIRKIN, C. A., Mechanistic study of photomediated triangular silver nanoprism growth. *Journal of the American Chemical Society* **2008,** 130, (26), 8337-8344.

[13] MAHAJAN, T.; MAHAJAN, A.; K. BEDI, R.; KUMAR, S.; SAXENA, V.; SINGH, A.; ASWAL, D., *Broadband enhancement in absorption cross-section of N719 dye using different anisotropic shaped single crystalline silver nanoparticles*. Journal? **2016**;. 6, issue? p 48064-48071.