

LOW TEMPERATURE SYNTHESIS OF SILVER NANOPARTICLES

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Abstract

The influence of lower temperature on size and polydispersity of silver nanoparticles prepared by reduction of the silver(I) diamine complex cation by sodium borohydride was studied. The preparation was carried out in ethylene glycol and ethanol in the presence of stabilizing agents. Silver nanoparticles were characterized by UV-Vis spectroscopy, dynamic light scattering (DLS) and transmission electron microscopy (TEM). The best results were achieved in ethanol. The smallest nanoparticles were prepared at the reaction temperature of -5 °C (3.4 ± 1.7 nm). With decreasing temperature, the average size of silver nanoparticles increased up to 7.2 ± 2.9 nm (-25 °C).

Keywords: Silver, nanoparticles, low temperature, preparation

1. INTRODUCTION

Present period of intense progress of nanotechnology brings a new life to materials, which have been used for centuries - materials, which enabled establishment of a significant branch of physical chemistry - the colloid chemistry. Colloid metal particles or currently more often labelled as nanoparticles always played an important role in technology, especially in the process of glass and ceramics dyeing [1], where gold colloids were of primary importance. The last quarter of the 20th century was characteristics with the renaissance of interest in metal colloid particles, especially due to the discovery of surface enhanced Raman scattering (SERS) [2], which initiated rapid development of the novel, highly sensitive spectroscopic technique enabling studies of single molecule [3]. The interest in silver nanoparticles (Ag NPs) as antibacterial agent is also worth mentioning as growing resistance of bacteria against antibiotics proves to be a key obstacle for the medicinal practice in the future [4]. Silver is probably the most frequently studied metal in the area of nanomaterial chemistry from the point of view of both unique physicochemical properties and area of application. However, the task of the preparation of silver nanoparticles with desired properties is far away from being completely solved.

Contemporary intense development of „wet processes“ commonly used in the Ag NPs preparation is closely connected with its SERS application. This area was pioneered by Creighton, Blatchford a Albrecht who prepared the silver particles using the reduction of AgNO_3 with a strong reducing agent ($\text{Na}[\text{BH}_4]$) in ice cooled aqueous medium [5]. The resulting nanoparticles were in the diameter from 5 - 20 nm with the absorption maximum („surface plasmon“) located at approx. 400 nm. The second, from already well-established reduction processes, is known as Lee and Meisel's process which uses weaker reducing agent, the citrate anion [6]. The citrate anion has additional function to stabilize silver nanoparticles in the course of their formation [7]. The reduction process is completed after boiling the reaction mixture for one hour; the prepared nanoparticles are significantly bigger and of higher polydispersity than nanoparticles prepared using borohydride as the reduction agent. Their diameters range from 30 to 120 nm, their surface plasmon is located at approx. 420 nm and the stability of the dispersion is limited, when compared to the borohydride process. Therefore, borohydride reduction method offers more reliable fabrication of small and stable Ag NPs. However, reproducibility of this process is lower and strongly dependent on the good laboratory experience. The aspect of reproducibility can be positively influenced using appropriate stabilizers. However, the addition of a modifier

in the course of the reduction can result in a certain increase in the particle diameter (when compared to the original process) [8]. Therefore, the idea of the lower temperature application could represent a solution how to increase reproducibility of the reduction process with the result of production of particles under 10 nm in diameter. Unfortunately, conducting of the reduction in aqueous environment is limited with the freezing point of water. Lowering the reaction temperature under 0°C could be achieved only with anti-freezing mixture of water with alcohols. This mixture and also pure alcohols are often used as non-aqueous environment for Ag NPs production. The alcohols are weak reduction agents. Therefore, they can be used directly for production of Ag NPs without utilization of any other reduction agent, especially under elevated temperature. Polyols are used in this way for preparation of the Ag NPs. The stability of the nanoparticles in non-aqueous environment is low and suitable stabilizers should be used for prevention of the aggregation. Typically, Ag particles prepared in ethyleneglycol at 180°C are due to aggregation bigger than 1 µm. This particle diameter, however, steeply decrease to 50-80 nm when polyvinylpyrrolidone (PVP) is used as polymeric stabilizer [9]. This size could be additionally lowered down to 10 nm when ammonia was used as a complexing agent [10]. Also simple alcohols can be used directly as reducing agent. Typically, ethanol can reduce Ag⁺ directly to Ag NPs and on the contrary to the polyols the reduction process can be conducted at laboratory temperature. of course, utilization of the stabilizers as PVP is necessary also in this case [11,12]. Nanoparticles with diameters below 10 nm can be produced by following the same preparative process when some specific stabilizers are applied. Ag NPs in diameter range from 5 up to 100 nm can be produced via solvothermal synthesis in ethanol and under the support of dodecanethiol stabilization (unfortunately, this compound strongly inhibited the surface activity of the Ag NPs) [13]. Application of stabilizers from the group of non-ionic surfactants (Brij, AOT, Tween) is connected with synthesis of Ag NPs with size under 10 nm (6-10 nm) performed under laboratory temperature [14], and the application of latex microparticles as stabilizers in combination with microwave synthesis resulting in fabrication of Ag NPs in the diameter range 5-10 nm (note: the system exhibit high polydispersity) [15]. The smallest Ag NPs were prepared using aminosilanes as stabilizers - the diameter range was 1-3 nm under elevated temperature (30-60°C). Several studies were also conducted in ethanol environment using e.g. hydrazine as a reducing agent to produce stable Ag NPs (stabilized by PVP) but the obtained particles were in the diameter range 50-70 nm [16]. Also studies employing photons as initiator of the reduction process were published - γ-radiation proved to be more effective (Ag NPs fabricated were in the diameter range 15-35 nm) [17] than visible light (diameter in the range 20-100 nm) [18].

In spite of the number of the above mentioned studies, none of them was aimed on utilization of temperature lower than 0°C as a key condition for a reproducible production of truly small (under 10 nm) Ag NPs. Therefore, the study of the influence of the temperature under the freezing point of water became the main task of the presented study.

2. EXPERIMENTAL

Silver nanoparticles were prepared via the reduction of silver(I) diamine complex cation [Ag(NH₃)₂]⁺ using sodium borohydride as a reducing agent. 50 % v/v ethanol was used as reaction medium to have possibility conduct the reaction down to -25 °C. 5 mL of 5 mmol/L aqueous solution of AgNO₃ (p.a., Sigma Aldrich) was mixed in a baker with 5 mL of 25 mmol/L ethanolic solution of ammonia (p.a., Sigma Aldrich) and 2.5 mL of 1 % w/w aqueous solution of polyacrylic acid (M_r=1,200, Sigma Aldrich). The reaction mixture was cooled down to reaction temperature in cryostat after adding additional ethanol (7.5 mL, UV purity, Sigma Aldrich) and water (4 mL). After the adjustment of the temperature, the reaction was started through the injection of 1 mL of precooled 5 mmol/L aqueous solution of NaBH₄ (p.a., Sigma Aldrich) using injection rate 0.2 mL/min. Although the reaction rate decreased with decreasing temperature, it was anyway completed after 10 min from the injection of the reducing agent which was indicated by stable yellow color of the reaction mixture. The reaction mixture was stirred using external stirrer with glass propeller the whole reaction time. All used solutions were prepared with deionized water (18 MΩ·cm, Millipore).

After completing of reaction the reaction mixture was taken out from cryostat and was kept freely on the air to reheat it to the room temperature. Then the prepared dispersion of nanoparticles was characterized using UV-vis spectroscopy (Specord S 600, Analytik Jena AG, Germany) in 1 cm cuvette after 5 times diluting by water, dynamic light scattering (DLS) on Zetasizer Nano ZS (Malvern Co., UK), and transmission electron microscopy (TEM) on JEM 2010 (Jeol, Japan) instrument.

Catalytic activity of the prepared nanoparticles was evaluated using a model reaction based on the reduction of methylene blue (MB) by NaBH₄. The reaction course was monitored via the UV-vis spectroscopy thanks to the observation of the intensive absorption peak of the oxidized MB form at the wavelength of 664 nm. The catalytic experiments were performed directly in the spectroscopic cuvette under laboratory temperature. 1 mL of 10 µmol/L aqueous solution of MB in ammoniacal buffer (pH=10) was pipetted to the cuvette with 10 µL of the prepared nanoparticle suspension and 1 mL of water. The reaction was started through a quick injection of 1 mL of 0.5 mmol/L aqueous solution of NaBH₄. During reaction course, spectra of the MB in the interval 360-760 nm were acquired in the regular time intervals. The evaluation of the kinetic data was performed using values of maxima absorbance MB from the recorded spectra using approximation of the 1. order kinetic equation.

3. RESULTS AND DISCUSSION

The used preparation method for Ag NPs is based on the previously mentioned Creighton, Blatchford a Albrecht borohydride method in combination with Tollens procedure where silver(I) diamine complex cation is used as silver source instead simple silver cation. Additionally, polymeric stabilizer (polyacrylic acid) was used as adjuvant in reaction mixture to avoid a problem produced Ag NPs aggregation in mixed environment water-ethanol (1:1). Thanks to low freezing point of this solvents mixture the preparation procedure could be proceeded at temperatures down to freezing point of pure water. In our experiments we have tested three reaction temperatures: -5, -15 and -25 °C. Lowering of the reaction temperature was accompanied with decreasing of the reaction rate of the studied redox reaction. The first change of colour of the reaction mixture (it is colorless) was observed immediately after mixing of reaction component at temperature -5 °C. At -15 °C the first colour change was observed approximately after 30 s from the point of mixing of reaction components and at -25 °C this time was prolonged to about 60 sec. This change in reaction rate is probably a reason for change of diameter of the emerged Ag NPs as was observed primarily from DLS measurements (see **Table 1**) and consequently also from TEM pictures (**Figure 1**). The real size distribution of diameter of the prepared Ag NPs was evaluated from these TEM micrographs and their graphical representations are presented on **Figure 2**. Average values of diameters of the prepared Ag NPs at different reaction temperatures evaluated from the size distribution are presented with values of polydispersity in **Table 1**. The extraordinary difference between average values of Ag NPs diameters determined from DLS and from TEM are clearly visible in **Table 1**. The abnormally big diameters determined from DLS are very probably connected with presence of polymeric stabilizer which can interconnect prepared Ag NPs to weakly bonded bigger objects which can be stable only in liquid environment and not on dry microscopic grid. The existence of this bigger object is clearly visible also from the UV-vis spectra at which two absorption maxima are observed. The first located below 400 nm is connected with localized surface plasmon of individual particles while emergence of second absorption maxima at about 450 nm is caused by existence of weakly interconnected nanoparticles. Therefore, the real diameters can be evaluated only from TEM micrographs. And from them a clear dependence on the reaction temperature is visible. Lowering of reaction temperature results in growing of average diameters of the prepared Ag NPs. The reason of this dependency is clearly connected with the change of the reaction rate in initiation part of reaction curve. The reduction procedure for preparation of metal nanoparticles is typical example of the autocatalytic reaction. The reaction curve for this type of reaction has a typical S shape. At the start of reaction nuclei of new metal phase are formed by slow homogeneous mechanism. However, when first stable nuclei are formed the second reaction phase of quick catalytic growth of the particles is rapidly getting on. Homogeneous mechanism formation of stable nuclei is strongly temperature dependent due to high

activation energy. Therefore, with lowering temperature less nuclei are formed at the initiation period and final diameter of Ag NPs is bigger due to large amount of silver ions which are left for reduction on individual nuclei during quick catalytic step. It is also important to note improvement of polydispersity of the prepared disperse systems of Ag NPS with lowering of reaction temperature which is also very probably caused by the slowdown of the reaction rate in the initiation step of the whole autocatalytic reaction. Due to high reaction rate in catalytic step of the reaction mechanism silver cations are quickly exhausted and first initiation step is suppressed by this way. When new nuclei are not formed during reaction steps after initiation period polydispersity of the emerging system is improved.

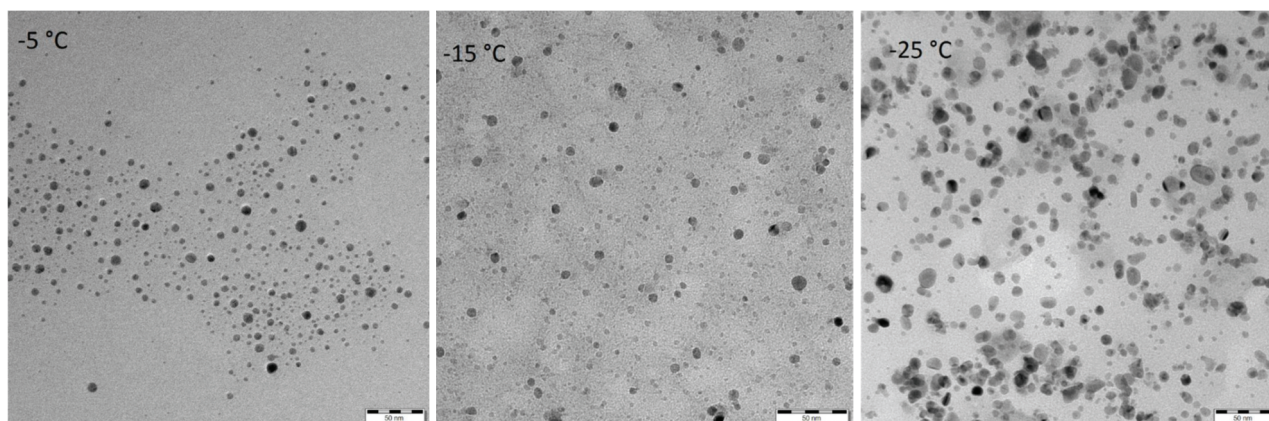


Figure 1 TEM micrographs of Ag NPs prepared by reduction $\text{Ag}[\text{NH}_3]_2^+$ by borohydride in the presence of PAA as stabilizer at different temperatures below freezing point of water

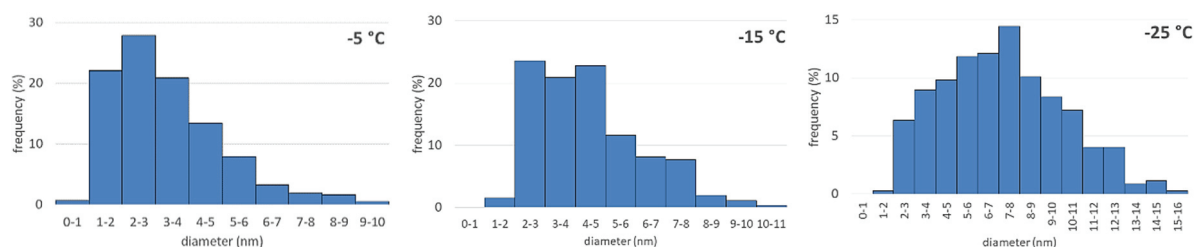


Figure 2 Distribution diagrams determined from TEM for Ag NPs prepared by reduction $\text{Ag}[\text{NH}_3]_2^+$ by borohydride in the presence of PAA as stabilizer at different temperatures below freezing point of water

Very small silver nanoparticles prepared via the newly proposed method can have promising properties, especially thanks to its perspective catalytic activity. As it can be concluded from numerous published catalytic studies, aimed on the evaluation of catalytic activity of the metal nanoparticles, the smaller the nanoparticles are, the high catalytic activity can be expected. The simple catalytic experiments using model reaction of reduction methylene blue (MB) with borohydride were conducted to confirm this conclusion also in the case of so small nanoparticles as were prepared in this study. In course of the reaction, the spectrum of MB was taken at certain time intervals and after the reaction end the values of the absorbance at maximum for MB were evaluated and these obtained kinetic data (**Figure 3**) were processed using approximation of kinetics of the first order (big excess of borohydride in comparison with MB). The reference measurement of the used model reaction was made without Ag NPs as the catalyst - in this case the apparent rate constant was 0.0035 s^{-1} , which is significantly lower (minimally one order) in comparison with the lowest apparent rate constant for the slowest reaction catalyzed with the prepared Ag NPs (see values of k_{aoo} in **Table 1**). The obtained kinetic data confirm growing catalytic activity of the metal nanoparticles with decreasing of their diameter. In our case, this conclusion is valid for the Ag NPs with diameter 3.4 nm, which one approximatively contents 10^3 Ag atoms.

Therefore, for Ag NPs, containing minimally 10^3 silver atoms, the main rule about the dependence of catalytic activity of Ag NPs on their diameter is fulfilled.

Table 1 The values of average diameters and maxima of absorbance from UV-vis spectra for Ag NPs prepared by reduction $\text{Ag}[\text{NH}_3]_2^+$ by borohydride in the presence of PAA as stabilizer at different temperatures below freezing point of water

T [°C]	TEM		DLS		UV-vis		k_{app} [s ⁻¹]
	diameter [nm]	polydispersity	diameter [nm]	polydispersity	1 st peak [nm]	2 nd peak [nm]	
- 5	3.4±1.7	0.250	115	0.189	342.5	451.5	0.1236
-15	4.4±1.8	0.167	59	0.083	344.0	445.0	0.0541
-25	7.2±2.9	0.162	50	0.022	344.5	446.0	0.0415

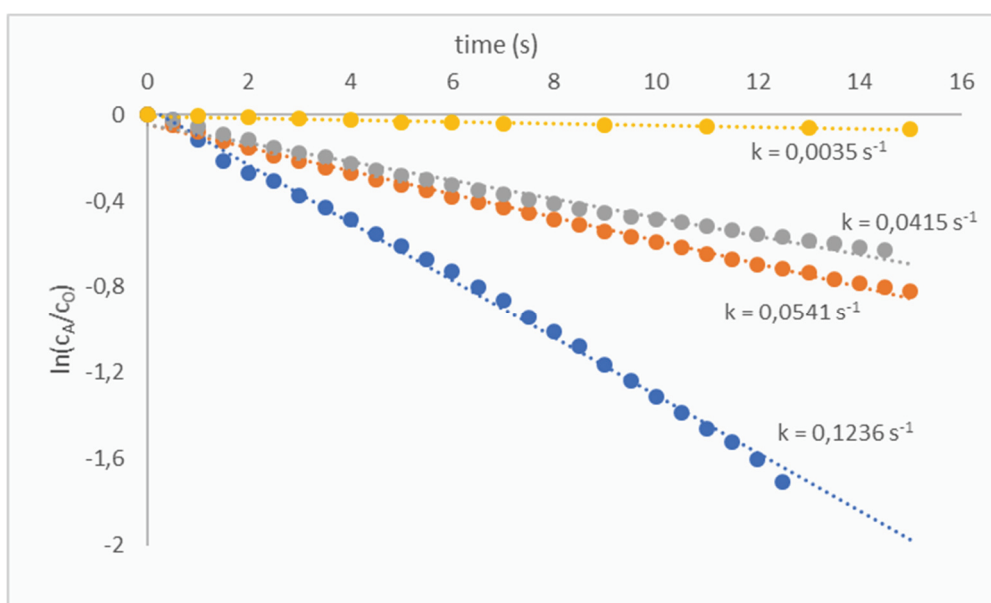


Figure 3 Kinetic curves for the reduction of methylene blue with borohydride catalyzed with the Ag NPs prepared at different reaction temperatures via the reduction of $\text{Ag}[\text{NH}_3]_2^+$ with borohydride in the presence of PAA as stabilizer

4. CONCLUSION

The reported study confirmed a possibility to tailor of the diameter and polydispersity of the silver nanoparticles prepared via a reduction method due to the change of reaction temperature, i.e. decrease of the reaction temperature below the freezing point of water. The average diameter of the prepared Ag NPs increased with the decrease of the reaction temperature and simultaneously polydispersity is improved due to the slowed down reaction rate in initiation step of nuclei formation. The smallest prepared nanoparticles with average diameter 3.4 nm are the best redox catalyst as proved with the used model reaction of reduction methylene blue by borohydride, which is in accordance with other studies aimed at evaluation of influence of the nanocatalyst size on its catalytic activity.

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