

Glucose-assisted polyol synthesis of silver nanoplates and nanoprisms in the presence of oxyethylated carboxylic acid

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This paper belongs to the CTFM'22 Special Issue: <https://www.kaznu.kz/en/25415/page>.

Guest Editors: Prof. N. Uvarov and Prof. E. Aubakirov.

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Abstract

This work reports a simple route to synthesizing silver nanoplates and nanoprisms through a polyol approach in the presence of oxyethylated carboxylic acid and glucose. The resulting particles were characterized by electron microscopy and X-ray diffraction (XRD). The introduction of glucose and NaOH into the system substantially increases the yield of nanoplates and reduces their thickness. The optimized reaction conditions can be used to produce, in a one-pot synthesis, silver nanoplates and nanoprisms which may have applications as metallic fillers in ink and paste formulations for 2D and 3D printing to fabricate functional components and devices.

Keywords

silver
nanoprisms
ethylene glycol
glucose
reduction

Received: 24.06.22

Revised: 21.07.22

Accepted: 21.07.22

Available online: 03.08.22

Key findings

- Glucose promotes the formation of silver nanoplates and nanoprisms at room temperature and increases their yield.
- The silver nanoplates change the shape to nanoprisms with increasing temperature.
- In the presence of NaOH, the yield of plate-like structures and their aspect ratios increase.

1. Introduction

Over the last few decades, due to the increasing number of applications, conductive inks, pastes and adhesives for flexible printed electronics have received much attention [1, 2]. The metals most commonly used in the ink formulations are silver, copper, nickel, gold, aluminum and zinc. However, silver is the best choice for electrically conductive inks, pastes and adhesives because of its high electrical and thermal conductivity, chemical stability and the ability of its oxide form to show good conductivity [3].

Silver nanoplates and nanoprisms, a new class of nanostructures with two-dimensional anisotropy, have been of special interest for the applications in sensors and diagnostics because of their structure, optical, electronic, and catalytic properties that are generally superior to those of spherical nanoparticles of a comparable size [4, 5]. It was also shown that, after printing the inks based on non-spherical silver particles onto plastic substrates and subsequent annealing, the resultant Ag patterns are more uniform and show a lower resistivity and improved mechanical properties as compared to those of similar patterns prepared from spherical particles [6].

Different chemical and physical techniques are used to prepare silver particles, including chemical reduction of the silver ions in various media, various types of irradiation and electrochemical processes as well as solvothermal and polyol methods, etc. [7]. One of the most common solution-phase approaches to producing micrometer- and nanometer-scale silver particles is the polyol process in which the polyol acts both as the solvent and reducing agent. The advantages of the polyol process are that it is low-cost, easy to use, and scalable. It also allows control of the particles size and shape by varying reaction conditions, such as temperature, reduction time, the reagent concentrations, and type of stabilizer, resulting in the formation of different morphologies [4, 8].

Among other Ag anisotropic nanoparticles, triangular prisms and plate-like nanostructures are being extensively investigated [9]. The formation of anisotropic shapes is not thermodynamically favored; that is why, in order to promote anisotropic growth of silver nanocrystals, the use of structure-directing agents, which can selectively adsorb on different crystal facets, is required. In most of the reported methods, citrate and poly(vinylpyrrolidone) (PVP)

have been widely used as capping agents to induce the formation of silver anisotropic particles [10]. Xue et al. reported [11] that citrate ions both reduced silver ions and helped the formation of plate-structured Ag nanoparticles. Zhang et al. found that the list of ligands with selective adhesion to Ag (111) facets can be expanded from citrate to many other di- and tricarboxylate compounds [12]. In contrast to citrate, PVP binds more strongly to the (100) than (111) facet [13] and this selectively leads to the formation of Ag nanocubes. In addition to citrate and PVP, several other capping agents used to obtain anisotropic structures of silver have also been reported in the literature. Thus, in the presence of Br⁻ ions, the formation of silver nanocubes, rectangular nanobars, and octagonal nanorods is induced [14]. Silver microplates, with average edge length of about 1.5 μm and a thickness of 100 nm, were synthesized in the presence of *n*-octanol playing an important role in the formation of the plate-like structure [15]. Xiong et al. prepared silver nanoplates with a triangular or hexagonal shape by introducing polyacrylamide (PAM) when reducing silver nitrate with ethylene glycol [16]. However, it is worth noting that the number of facet-selective capping agents which could be successfully used to prepare silver structures with different shapes is very limited.

Herein, we report the results of the study on the reduction of silver ions with ethylene glycol in the presence of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA) and glucose aiming to develop a simple method to prepare silver nanoplates. The proposed method has advantages in terms of both cost and ease of implementation; it does not require unique and expensive equipment and can be used for large-scale production of silver powders.

2. Experimental

2.1. Reagents

Silver nitrate (AgNO₃), 99.9% purity grade, SoyuzKhimProm, Russia), 2-[2-(2-methoxyethoxy)ethoxy] acetic acid (C₇H₁₄O₅, MEEAA) of 95% purity grade (Sigma Aldrich, USA), ethylene glycol (HO(CH₂)₂OH, EG) of 99.9% purity grade, 95% pure ethanol supplied by Khimmed (Russia), and sodium hydroxide (NaOH, 50% aqueous solution) were used as received without further purification.

2.2. Synthesis of silver particles

The reduction of silver nitrate was carried out as follows. An appropriate amount of MEEAA was dissolved in 25 ml of ethylene glycol, and then a stoichiometric amount of sodium hydroxide was added to the solution under stirring. Silver nitrate was dissolved in ethylene glycol and added to a solution of the sodium salt of MEEAA in ethylene glycol under constant stirring. After stirring for 5 min, the mixture was heated to the required temperature, followed by the addition of a solution of glucose in ethylene glycol. After the reaction was complete, the mixture was air-cooled and the supernate was decanted. The

resulting precipitate was washed three times with ethanol to remove the impurities and then it was dried in air at room temperature.

2.3. Characterization

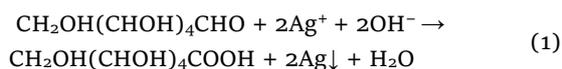
X-ray diffraction (XRD) patterns were recorded on a D8 Advance powder X-ray diffractometer equipped with a 1D Lynx-Eye detector and Ni-filtered Cu Kα radiation (0.02° 2θ step size and an accumulated time per step of 35.4 s). Phase identification was carried out using Powder Diffraction File (PDF) databases (ICDD, Release 2001). Analysis of the samples by transmission electron microscopy (TEM) was performed using a JEM 2010 electron microscope (JEOL, Japan) operating at 200 kV and having a resolution of 0.14 nm. Study of the samples by high-resolution scanning electron microscopy (SEM) was performed using a Tescan scanning electron microscope (Czech Republic).

3. Results and Discussion

Our earlier study showed [17] that the reduction of silver ions with ethylene glycol in the presence of the sodium salt of MEEAA proceeds extremely slowly and leads to the formation of silver nanoparticles of 2–5 nm in size with a very low yield. An increase in the temperature up to 40 °C resulted in the formation of triangular and hexagonal silver nanoplates with edge lengths ranging from 100 to 200 nm and with a thickness of approximately 30 nm, but their yield was too low. A further increase in the temperature to 60–100 °C produced a sample containing irregularly shaped polyhedrons and a very small fraction of plates. In the present study, we attempted to produce Ag nanoplates with controlled shapes in high yields by adding glucose in the polyol synthesis.

As shown in this study, the addition of glucose (Glu) in the synthesis of silver nanoparticles in a mixture of ethylene glycol and sodium salt of MEEAA (NaR) affects the yield of silver nanoplates. Thus, at an Ag⁺:NaR:Glu molar ratio of 1:3:2 at a temperature of 30 °C and a synthesis time of 72 h, the yield of plates was 57%, and their size and thickness were 240 and 40 nm, respectively (Figure 1a). It should be noted that, under similar conditions but at a lower Ag⁺ to Glu molar ratio of 1:1, the final product contained 40% of the plates, with mean sizes of 170 nm in edge length and 25 nm in thickness, while the remaining 60% were polyhedral shaped silver nanoparticles. Therefore, a decrease in the glucose content in the system decreases the yield of nanoplates, their length and thickness. At a molar ratio of glucose to silver of 1:4, under the same conditions, the final product contained 60% of plates with an edge length of 130 nm and a thickness of 40 nm, while the remaining 40% of silver nanoparticles were polyhedra (Figure 1b). A further increase in the ratio of Ag⁺:Glu to 1:6 led to a decrease in the nanoplate yield to 50%. The average thickness of these nanoplates was found to be approximately 30 nm, while their edge length was around 200 nm.

It is known [18] that, as pH increases, the value of the redox potential of glucose decreases, which means that, in an alkaline solution, its ability to donate electrons increases. As Raveendran et al. reported [19], the reason for this is that the base facilitates the opening of the glucose ring by the abstraction of the α -proton of the sugar ring oxygen and thereby speeds up both the oxidation of glucose to gluconic acid and the reduction of silver ions to silver atoms. Gluconic acid, the glucose derivative resulting from its oxidation, was reported to form a dense coating on the surface of nanoparticles, thereby stabilizing them [20]. In the presence of NaOH, the reduction reaction can proceed according to equation (1):



In order to promote the formation of plate-like structures, it was of interest to investigate the effect of alkali on the reduction of silver ions in ethylene glycol in the presence of glucose. In the synthesis, which was conducted at 30 °C and at an $\text{Ag}^+:\text{NaR}:\text{Glu}$ of 1:3:2, with the molar ratio of Ag to NaOH equal to 1:0.1 in the reaction mixture, an increase in the nanoplate yield to 70% was observed. The average edge length of the nanoplates and their thickness were 159.7 ± 68.2 and 25 nm, respectively (Figure 2a). Therefore, in the presence of NaOH, the yield of plate-like structures and their aspect ratios were higher than that obtained from the reduction in the absence of NaOH. It should be noted that an increase in the glucose concentration in the reaction system did not lead to any further increase in the nanoplate yield, and it remained at 60%.

The effect of temperature on the morphology of silver particles formed in the presence of glucose was studied. It was shown that an increase in temperature from 30 °C to 40 °C led to an increase in the thickness of the silver plates (Figure 2b). Thus, at an $\text{Ag}^+:\text{NaR}:\text{Glu}$ molar ratio of 1:3:2, uniform nanoprisms are formed with an edge size of about 150 nm and a thickness of about 70 nm. The reaction yield of the silver nanoprisms was 90%. Under similar conditions but at a lower Ag^+ to Glu molar ratio of 1:1, the yield of the silver nanoplates and their thickness also tend to increase as compared to those formed at 30 °C. Thus, as the temperature is increased, the Ag nanoplates become thicker and are finally transformed into nanoprisms. The same trend was observed to take place when reducing silver ions with ethylene glycol in the presence of the sodium salt of MEEAA alone [22].

The X-ray diffraction (XRD) pattern of the sample prepared under these conditions is shown in Figure 3. As seen, it has four diffraction peaks at $2\theta = 38.08^\circ$, 44.26° , 64.36° , and 77.52° attributed, respectively, to the diffraction from the {111}, {200}, {220}, and {311} planes of the face-centered cubic (FCC) lattice of silver (JCPDS, card no. 01-071-4613).

4. Conclusions

Triangular and hexagonal silver nanoplates were synthesized by reduction of silver ions with ethylene glycol in the presence of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA) and glucose. Compared with MEEAA alone, adding glucose promotes the synthesis of silver nanoplates and nanoprisms at room temperature and increases their yield. When the temperature is increased, the silver nanoplates were found to undergo a shape transformation to nanoprisms. The addition of NaOH to the reaction mixtures increases the yield of plate-like structures and their aspect ratios. The proposed method does not require unique and expensive equipment; it is low-cost and can be used for large-scale production of silver powders.

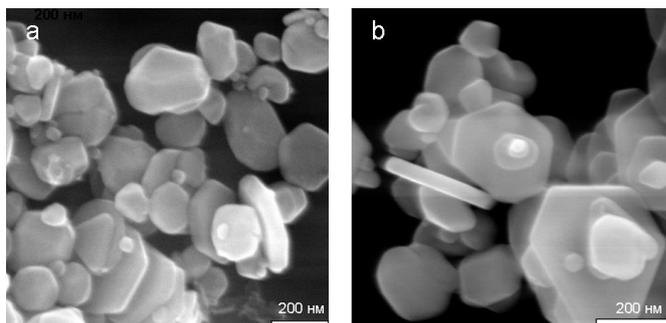


Figure 1 Micrographs of the silver nanoparticles prepared in the presence of glucose. $\text{Ag}^+:\text{NaR} = 1:3$, $T = 30^\circ\text{C}$, $\tau = 72\text{ h}$; $\text{Ag}^+:\text{Glu} = 1:2$ (a) and 1:4 (b).

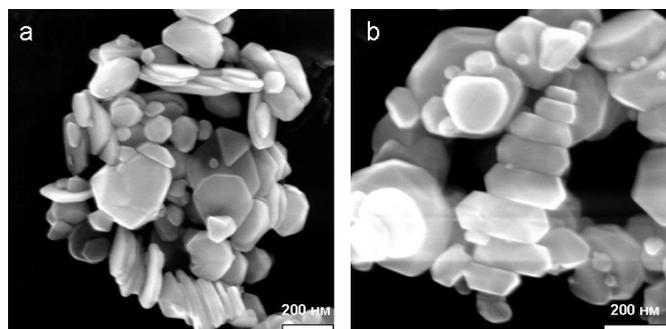


Figure 2 Micrographs of the silver nanoparticles prepared in the presence of glucose. Effect of pH (a) and temperature (b) on the size of silver nanoplates. $\text{Ag}^+:\text{NaR}:\text{Glu} = 1:3:2$, $T = 30^\circ\text{C}$ (a) and 40°C (b), $\tau = 72\text{ h}$; $\text{Ag}:\text{NaOH} = 1:0.1$ (a) and 1:0 (b).

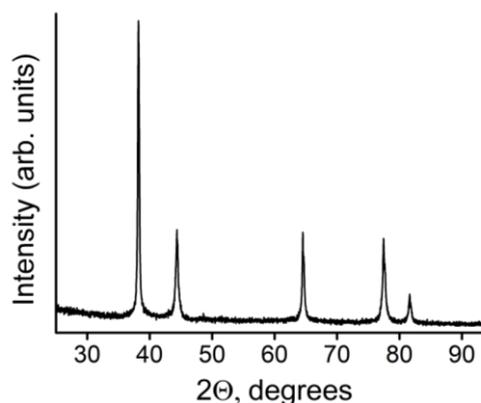


Figure 3 X-ray diffraction pattern of the silver nanoparticles prepared in the presence of glucose. $\text{Ag}^+:\text{NaR}:\text{Glu} = 1:3:2$, $T = 30^\circ\text{C}$, $\tau = 72\text{ h}$; $\text{Ag}:\text{NaOH} = 1:0.1$.

Supplementary materials

No supplementary materials are available.

Funding

The research was funded within the state assignment to ISSCM SB RAS (Project No. 122032900069-8).

Acknowledgments

None.

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Conflict of interest

The authors declare no conflict of interest.

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