Materials Physics and Mechanics 32 (2017) 198-206 Received: August 16, 2017

SYNTHESIS OF SILVER NANOCHAINS WITH A CHEMICAL METHOD

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Abstract. We describe the method of synthesis of chain-like silver nanowires (nanochains) and find the favorable conditions to fabricate them. The nanochains are processed in the hot ethylene glycol solution with constant stirring in the presence of nickel nanoparticles and polyvinylpyrrolidone 360000 molecules. Silver nanochains consist of straight-linear segments connected end-to-end. The length of straight-linear segments is from 100 to 500 nm, the diameter is about 80 nm; the angle between segments varies from 30 to 90°. The total nanochain lengh reaches 100 microns. The mechanism of silver nanochain formation is discussed.

Keywords: chain-like silver nanowires; silver nanowires; chemical synthesis of nanostructures; metal nanoparticles.

1. Introduction

Silver nanowires (AgNWs) belong to the class of one dimensional nanomaterisls (1D), together with carbon nanotubes, semiconductor nanorods and other [1]. The most promising application of AgNWs are in flexible electronics, optoelectronics, photovoltaics and sensorics [2-5]. Properties of AgNWs depend on their morphology and size that can be influenced by changing of synthesis conditions or coating with additional shells on the surface of nanowires [6].

In general, methods to fabricate metal nanowires can be subdivided into physical and chemical ones [7]. While physical methods allow to get nanowires without chemical reactions, chemical methods imply production of metal nanowires by chemical transformation starting from metal precursor and ending with atom agglomeration into nanoobjects. Among physical methods one can mention physical vapor deposition, electrodeposition through a porous membrane or synthesis by control of electrical charging, polarization and electrochemical potential [8-10]. Chemical reduction of silver ions is the most well-known method, which is often used to fabricate AgNWs [11]. Variation of conditions of AgNW synthesis, such as temperature, molar fraction of surfactants and duration of synthesis process influence the morphology of resulting nanoobjects.

In many cases, the reduction takes place in liquid solutions that act as the media for the chemical process. Ethylene glycol (EG) is usually used as such a liquid, but there are other substances, which serve the same purpose, e.g. water, N,N-dimethylformamide (DMF) and other [12, 13]. EG can be both a reduction agent and a capping agent, whereas water normally is only the carrier medium for chemical reactions. On the other hand, synthesis of AgNWs in water solution can be implemented in the presence of surfactants as capping agents. In some cases, additional chemical acts as both a reduction and a capping agent. For example, aromatic molecules, vitamin C or plant extract demonstrate such properties in water solution [14-16].

Employment of clove oil as medium for chemical reduction is another rather exotic was to AgNW synthesis [17]. Clove oil consists of many substances that provide reduction and capping properties. Synthesis of AgNWs in EG solution can be implemented at higher temperatures (about 180 °C) compared to aqueous synthesis, increasing the duration of synthesis process. However, there are methods that allow to bring down the reaction time, e.g. microwave-polyol method [19].

Choose of surfactant strongly influences the size and morphology during fabrication of AgNWs. Usually polyvinylpyrrolidone (PVP) is used as surfactant. The length of PVP molecule regulates the length of a silver nanowire. Molecular weight of PVP is 1300000 g/mol that determines the length of hydrocarbon skeleton of PVP molecule, which reaches 2 microns. PVP allows to synthesize AgNWs up to several microns length. Besides PVP other surfactants are used to make AgNWs, such as poly(diallyldimethelammonium)chloride (PDA) and dibutyl sebacate (DBS) [20, 21]. DBS allows to fabricate nanobelt structures, which demonstrate thickness about 20 nm, width about 60 nm and are several microns of length [21]. Silver nanorods fabricated fabricated in the presence of PDDS have length about 100 nm and diameter about 25 nm [20]. Variation of molar fraction Ag/PVP influences the AgNW morphology, too. Change of molar fraction Ag/PVP decreases yield of silver nanowires ans aspect ratio [22, 23].

Synthesis of AgNWs in the presence of metal nanoparticles as the seeds allows to increase the yield of nanowires and the length of nanowires or fabricate the zigzag silver nanowires [24-26]. Increasing of seed size reduces number of silver nanowires. Zigzag silver nanowires are one dimensional nanoobjects, which consist of several straight-linear segments connected end-to-end [27]. Recently such silver nanoobjects have been accidentally observed, however the specific conditions for their synthesis have not been reported [28].

In the present work, we describe the synthesis of chain-like silver nanowires- silver nanochains (SNCs) in the presence of nickel nanoparticles as seeds and synthesis of silver nanowires in the presence of silver nanoparticles as seeds.

2. Experimental

2.1. Materials. We used Sigma Aldrich chemicals: silver nitrate (CAS # 7761-88-8), ethylene glycol (EG) (CAS # 107-21-1), polyvinylpyrrolidone (PVP) 10 000 and 360 000 (CAS # 9003-39-8), nickel acetate (CAS # 373-03-4), citric acid (CAS # 77-92-9), hydrazine-hydrate (CAS # 301-01-2) and distilled water.

2.2. Synthesis of silver nanopartilces (AgNPs). Fabrication of AgNPs was processed in two stages. At the first stage, the aqueous solution of silver nitrate and PVP were prepared. Silver nitrate (4.24 g) was dissolved in 25 ml of distilled water. PVP (2 g) 10 000 was dissolved in 200 ml of distilled water. At second stage, 1 ml of aqueous solution of silver nitrate and 0.03 ml of hydrazine-hydrate were dissolved in 200 ml of PVP aqueous solution at room temperature. Prepared solution was stirred during 20 minutes.

2.3. Synthesis of nickel nanoaprticles (NiNPs). Fabrication of the NiNPs was processed in two srages, too. At the first stage, nickel acetate (0.62 g) was dissolved in 25 ml of distilled water. Then 0.07 g of citric acid was dissolved in 25 ml of ethylene glycol. At the second stage, 0.5 ml of aqueous solution of nickel acetate was dissolved in ethylene glycol contained citric acid. Resulting solution was heated up to 160 °C and was stirred for 2 hours.

2.4. Synthesis of silver nanowires (AgNWs). Silver nanowires were made in two different routes: in the presence of silver (i) and nickel (ii) nanoparticles as seeds. Each case was processed in 5 ml ethylene glycol heated to 160 °C. In the first case, we dissolved 0.01 ml of silver nanoparticle solution, in the second case - 0.1 ml of nickel nanoparticles solution in a reaction flask. The next stages of synthesis were the same for both cases. We prepared two additional solutions: silver nitrate (0.42 g) in EG (25 ml) and PVP 360 000 (0.9 g) in EG (25 ml). Both additional solutions were added to reaction flask drop wise: 1 ml $AgNO_3$/EG and

1.6 ml PVP/EG.

2.5. Characterization. Resulting nanowires and nanopartilces were deposited onto the surface of silicon oxide plate. Then silicon oxide plates covered with nanoobjects were washed by the mixture of water and ethanol several times to remove excess PVP molecules and other products of chemical reactions. Nanowires and nanoparticles located on dried silicon oxide plates were studied in scanning electron microscopes (SEMs): FEI Novanano, USA and CarlZeiss Sigma, Germany. UV/Vis absorption spectrum of AgNP solution was recorded with Promecolab PE-5400 UV spectrophotometer, Russia. Structure studies of nanowires and nanoparticles were performed with a X-Ray diffraction (XRD), Shimadzu XRD 7000, Japan.

3. Results

3.1. Silver and nickel nanoparticles for silver nanowire seeding. AgNPs have size about 300 nm, but some nanoparticles reach 80 nm in diameter. UV/Vis adsorption spectrum shows plasmon peak 409 nm that corresponds to typical spectrum range of silver nanopatricle solution [29]. Size of NiNPs was about 80 nm. The shape of AgNPs and NiNPs was close to spherical. XRD spectrum of NiNPs shows crystal from of FCC nickel.

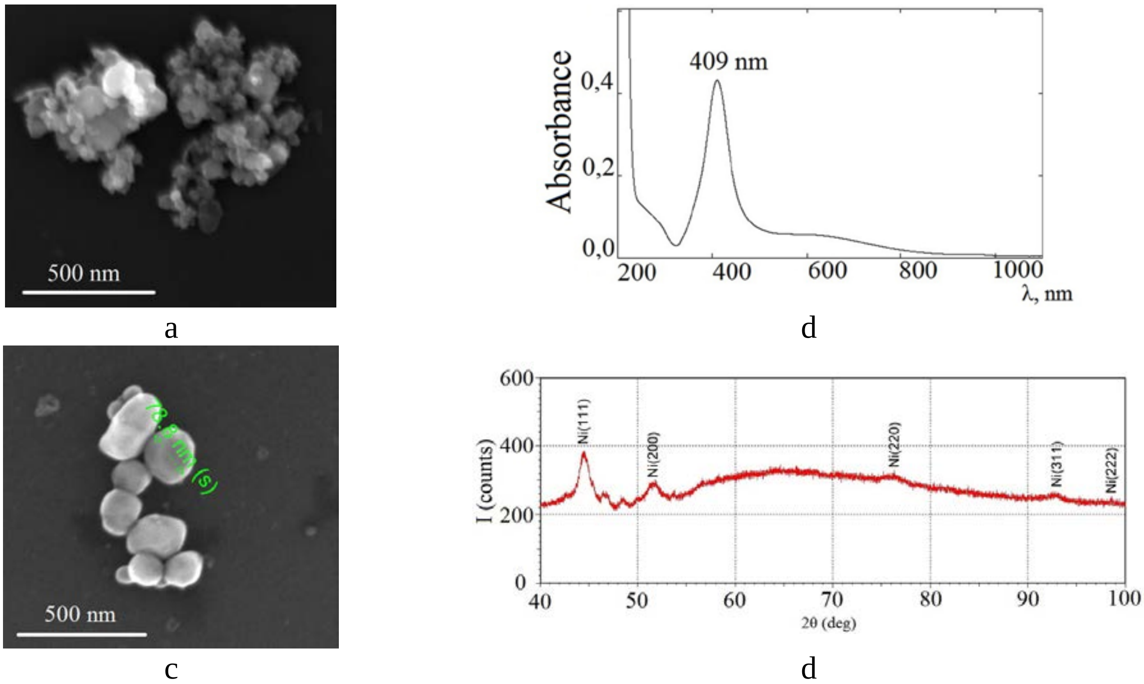


Fig. 1. Characteristics of resulting nanoparticles. (a) SEM images of AgNPs, (b) UV/Vis absorption spectrum of AgNP solution, (c) SEM images of NiNPs, (d) XRD spectrum of nickel nanoparticles.

We prepared two types of seeds: AgNPs and NiNPs, which were later used in the synthesis of silver nanochains. Figure 1 shows characteristics of the fabricated nanoparticles.

3.2. Synthesis of silver nanowires in the presence of silver nanopartilces

3.2.1. The role of temperature. Figure 2 shows the influence of synthesis temperature on the morphology of silver nanoparticles and nanowires. The synthesis temperature varied from 100 °C to 160 °C. Fabricated nanoobjects were characterized by SEM. At temperature below 120°C AgNPs were not observed. The size of AgNPs fabricated at 130 °C from 100 to 300 nm. Nanopartilces demonstrated close to spherical shape. Boost of temperature of synthesis allowed to increase the yield of silver nanowires was about 10 μm, diameter was about 120 nm, aspect ratio P ≈ 100.

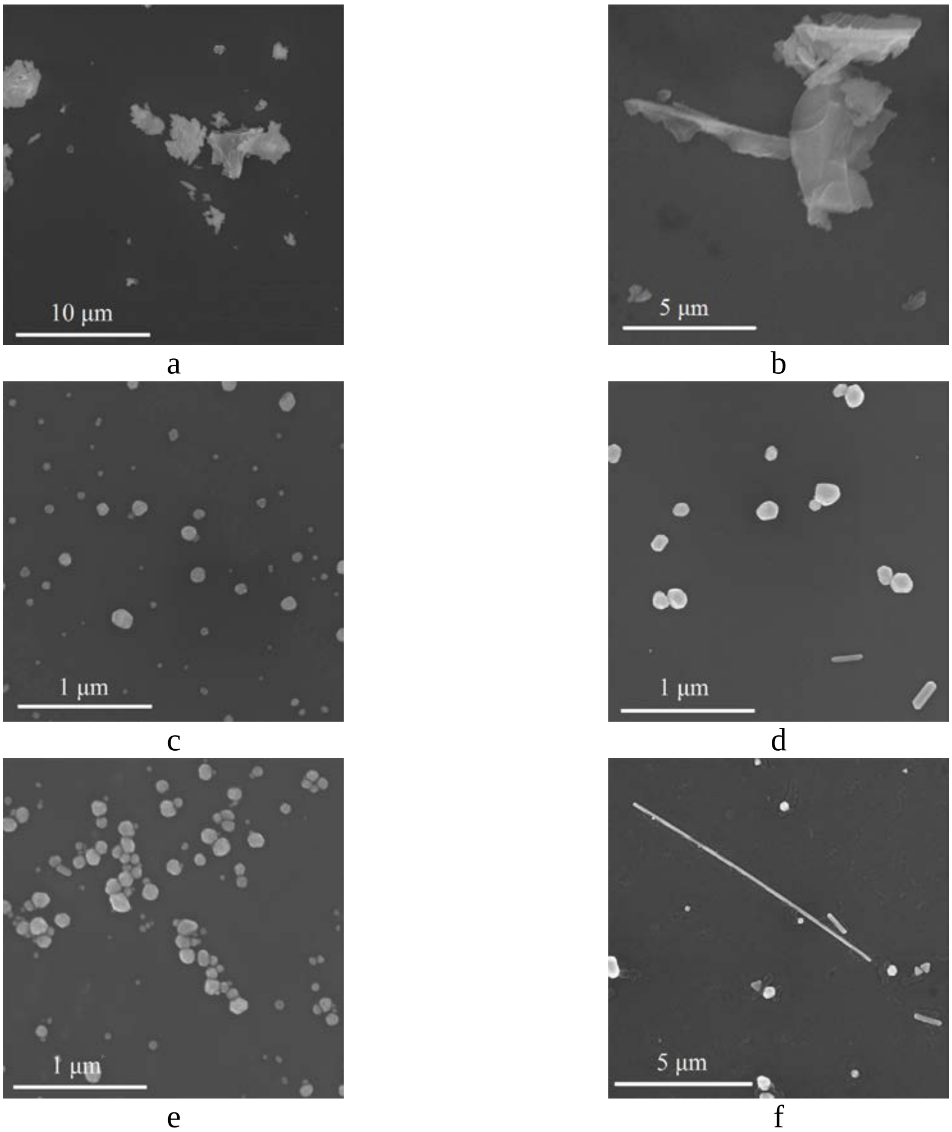


Fig. 2. Influence of synthesis temperature on the nanoobject morphology, SEM images: (a) 100 °C - absence of nanoobjects, (b) 110 °C - absence of nanoobjects, (c) 120 °C - spherical AgNPs, (d) 130 °C - spherical AgNPs, (e) 140 °C - spherical AgNPs, (f) 160 °C AgNWs, aspect ratio P ≈ 100. Reaction time for all experiments was 10 minutes.

3.2.2. The role of reaction time. Figures 3 and 4 show the morphology evolution of reaction time that changed from 20 to 80 minutes. At 130 °C the size of AgNPs increased from 50 to 150 nm. After 80 minutes of synthesis some nanorods were observed. The length of nanorods was about 170 nm, diameter was about 50 nm and aspect ratio P ≈ 3, respectively.

Silver nanowires were fabricated at 160 °C. Figure 4 shows increasing the length and aspect ratio of AgNWs. After 20 minutes of synthesis only AgNP were found, then after 40 minutes AgNWs were observed. The length of AgNWs was about 10 µm, diameter was about 100 nm, aspect ratio P ≈ 100.

3.2.3. Synthesis of silver nanowires in the presence of nickel nanopartilces. NiNPs serve as seeds for synthesis silver nanochains. Synthesis was processed in hot EG with constant stirring during 80 minutes. Ethylene glycol solution of silver nitrate and PVP/EG solution were added in the reaction flask drop wise. Nanoobjects were fabricated at two different temperatures: 130 °C and 160 °C. Figures 5 and 6 show silver nanoobjects prepared at 130 °C and 160°C, respectively.

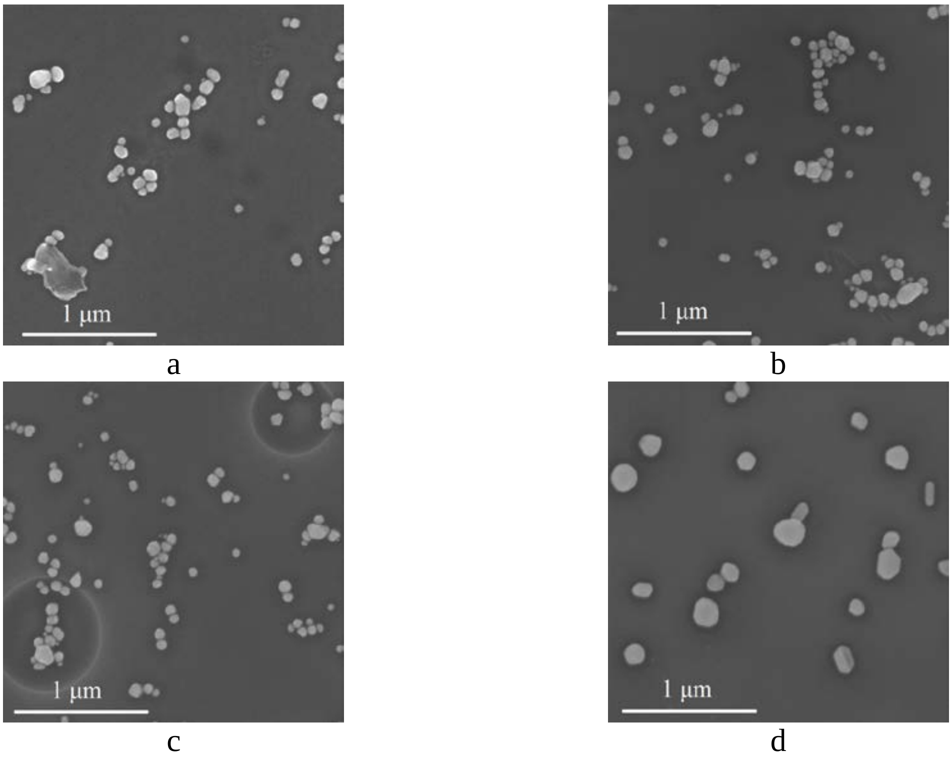


Fig. 3. Influence of reaction time on the morphology of nanoobjects at 130 °C, SEM images show spherical AgNPs with size depending on the synthesis duration: (a) 20 min, (b) 40 min, (c) 60 min, (d) 80 min.

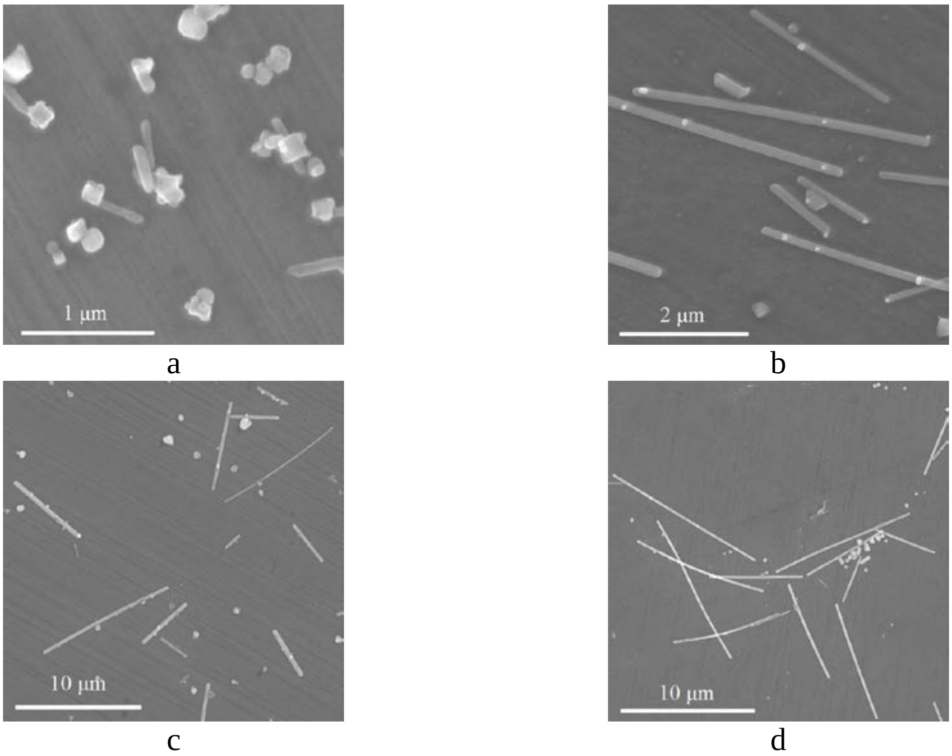
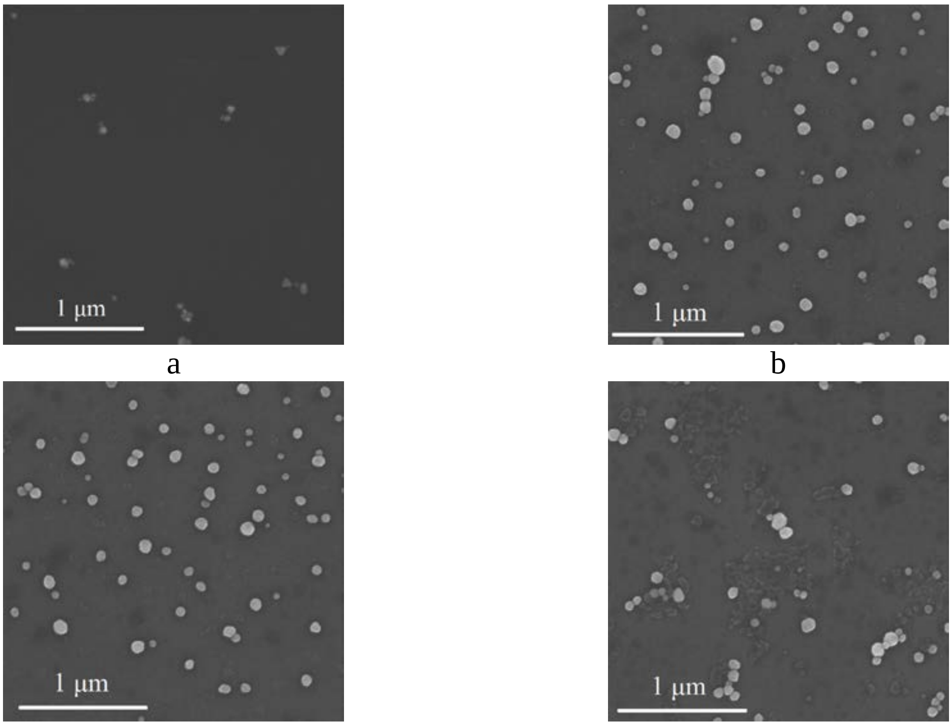


Fig. 4. Influence of reaction time on the AgNW morphology. Synthesis was processed at 160 °C; SEM images. Change of the aspect ratio (P) of AgNW: (a) 20 min olny AgNP; (b) 40 min, P = 15; (c) 60 min, P = 30, (d) 80 min, P =100.



a b
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Fig. 5. AgNPs fabricated in the presence of nickel nanoparticles at 130 °C. Process duration was: (a) 20 min (b) 40 min, (c) 60 min, (d) 80 min.

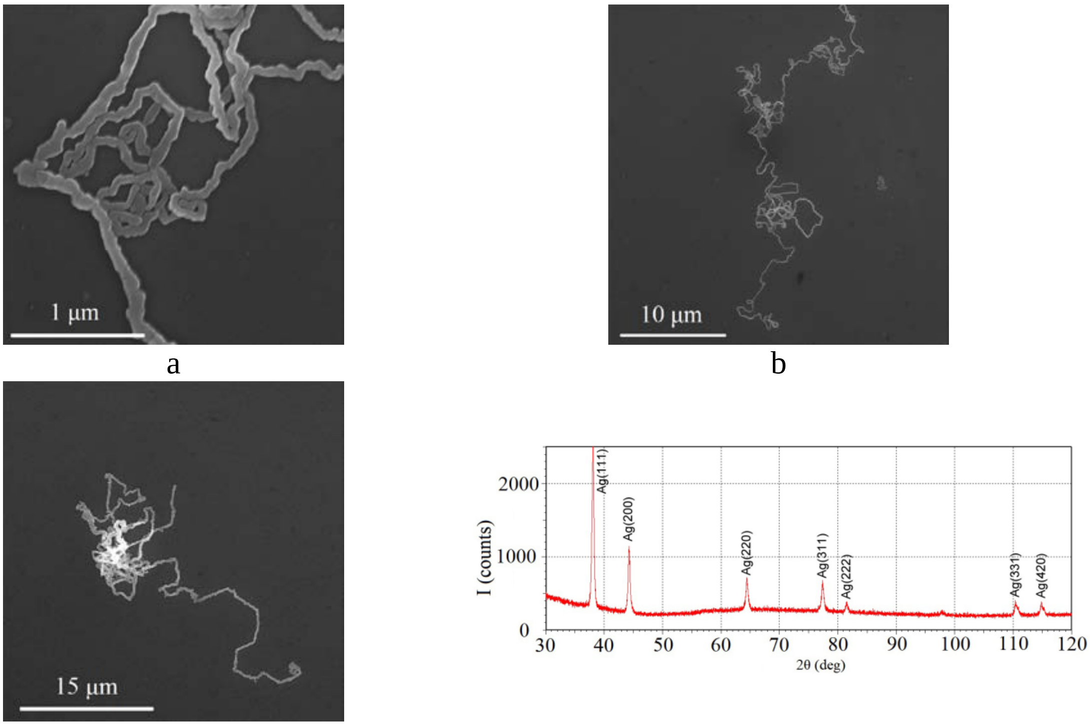

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Fig. 6. Silver nanochains in the presence of NiNPs: (a)-(c) SEM image of produced silver nanochains, P = 1000, (d) XRD spectrum of SNCs.

Nanopartilces processed at 130 °C had a spherical form. The size of AgNWs was about 50 nm. The yield of AgNPs increased during synthesis. AgNWs were not observed at 130 °C. Silver nanochains (SNCs) were found at 160 °C after 20 minutes of synthesis. SEM analysis showed SNCs diameter about 80 nm, the length - more 100 microns. XRD spectra of SNCs confirmed Ag FCC crystal form. SNCs (see Fig. 6) consist of straight-linear silver nanowire segments connected end-to-end. The length of straight-linear segments varied from 100 to 500 nm, angles between segments was about from 30° to 90°. The total length of silver nanochains was about 100 μm, diameter was about 80 nm. The number of silver nanochain bends was about 5 for each micron of length.

4. Discussion

We synthesized 1D nanoobjects, consisted of straight-linear silver nanowire segments, connected end-to-end, i.e. silver nanochains (SNCs). We found the optimal conditions for fabrication of SNCs. Silver nanochais were fabricated by chemical reduction of silver ions in ethylene glycol solution in the presence of nickel nanopartilces and molecules of polyvinylpyrrolidone (PVP) 360000 at 160 °C at 20 minute process with constant stirring. Silver nitrate and PVP are added to the reaction solution drop wise. The Table 1 presents the conditions for the synthesis of studied silver nanoobjects. We demonstrated that chemical reduction of silver ions takes place at temperatures higher than 130 °C. Silver nanowires were observed at 160 °C synthesis. There are no silver nanowires at the process temperature below 160 °C. Duration of synthesis influence the morphology and yield of silver nanoparticles and nanowires. Rise of synthesis duration boosts the yield of nanoobjects. Using nanoparticles as seeds defines the morphology of AgNWs, too. Metal nanoparticles act as growth centers and increase the yield of AgNWs. We suppose that increasing of reaction temperature changes adsorption properties of PVP molecules on surface of the growing nanoparticles, that allows to grow AgNW along the PVP molecule. The formation mechanism of SNC is schematically shown in Fig. 7. Chemical reaction of copolymerization between PVP and EG molecules takes place. NiNPs are catalyst for this chemical reaction unlike AgNP. Straight-linear AgNWs grow along the PVP molecules and connect each other. Accordingly, several straight-linear AgNW segments become connected connect end-to-end and turn into a silver nanochain.

In conclusion, the presented research gives the approach for synthesis of silver nanochains made of straight-linear silver nanowire sections. The developed approach can be used to create new 1D materials for flexible electronics.

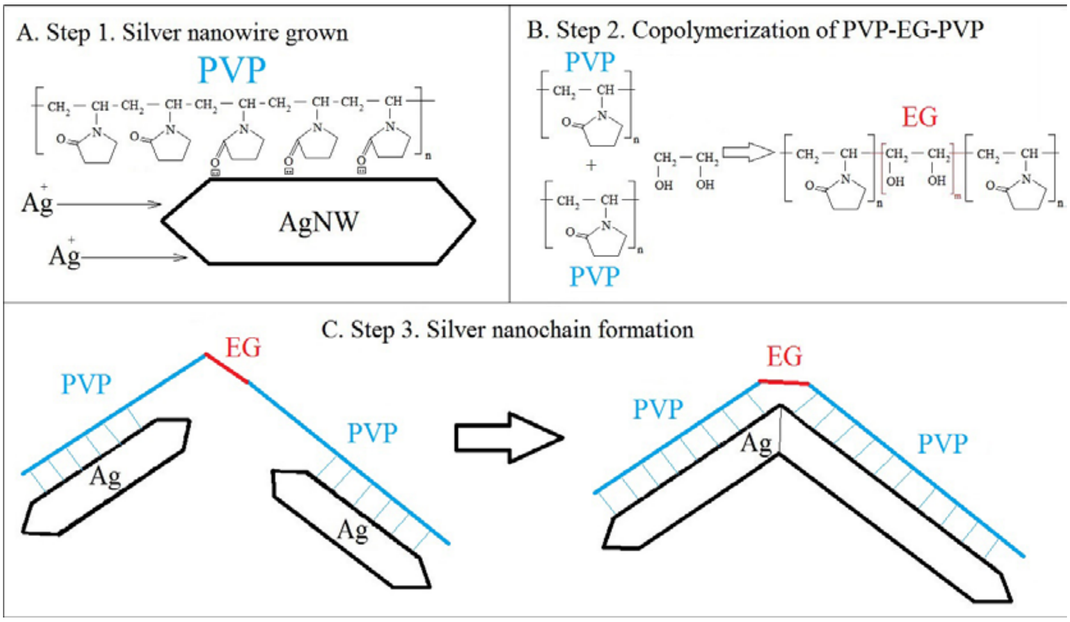

Fig. 7. Schematic illustration of the growth mechanism of silver nanochains: (A). Silver nanowires grown along the PVP molecules, (B) copolymerization PVP and EG in the presence of NiNP, (C) Formation of silver nanochain.

Table 1. Influence of synthesis conditions on the morphology of Ag nanoobjects.

Reaction time, min	AgNPs			NiNPs	
	Below 130 °C	130 °C	160 °C	130 °C	160 °C
20	Absence of nanoobjects	AgNP 300-500 nm	AgNP 100-200 nm	Spherical AgNP 20-30 nm	SNCs, the length - 100 microns,
40	Absence of nanoobjects	AgNP 300-500 nm	AgNP 300-500 nm and AgNW 120 nm, length	Spherical AgNP 20-30 nm	Synthesis was stopped
60	Absence of nanoobjects	AgNP 300-500 nm	AgNP 300-500 nm and AgNW 120	AgNP 40-60 nm	
80	Absence of nanoobjects	Synthesis was stopped	Synthesis was stopped	AgNP 80 nm	
Number of nanoobjects	Nanoobjects were not observed	Is not changed	Is not changed	Increases	Is not changed

Acknowledgements.

This work was supported by the Ministry of Education and Science of the Russian Federation, State Task 16.2314.2017/4.6 and by European Social Fund's Doctoral Studies and Internationalisation Programme DoRa.

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