Polyol synthesis of silver nanowires in the presence of silver chloride

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Silver nanowires have been synthesized by a modified polyol method, in the presence of silver chloride clusters previously obtained by the reaction between the silver precursor and sodium chloride. The effect of injection temperature and preparation conditions of silver chloride clusters and polyvinylpyrrolidone (PVP)/$AgNO_3$ molar ratio have been studied. Nanowires with an average diameter of 50 nm and aspect ratios above 100 have been obtained when the silver chloride clusters were formed at room temperature in the absence of PVP and injected into the reaction mixture at 160°C.

1. Introduction

One of the major challenges in the field of transparent conductive oxides is the replacement of expensive indium tin oxide with other transparent and highly conductive materials that can be used in the construction of flexible solar cells and different optoelectronic devices. Intensive research is still carried out on the synthesis and properties of alternative oxide materials, from which the most investigated candidate is undoped / doped zinc oxide [1-5]. Other possible substitute materials to the currently used indium tin oxide films are carbon nanotubes, graphene oxide, metal meshes and silver nanowires (AgNWs).

Silver nanowires have been attracting more and more attention because of their high electrical and thermal conductivity, mechanical flexibility and optical transparency. Properties of AgNWs are determined to a large extent by the shape, size, structure, and composition of these nanostructures, which in turn depend on the synthesis conditions [6-8].

Different synthesis methods have been used to produce AgNWs: chemical synthesis [9], hydrothermal method [10], DNA template [11], porous materials template [12], polyol process [13], and ultraviolet irradiation photoreduction techniques [14]. The polyol synthesis method is often preferred because a reasonable control on the AgNWs growth may be achieved by controlling some process parameters such as reaction time, molar ratio between capping agent and metallic precursor, temperature, and addition of control agent. The polyol synthesis method involves the reduction of silver ions by a polyol such as ethylene glycol to form metallic silver which forms clusters that act as seeds for the nucleation and growth of nanowires. A capping agent such as polyvinylpyrrolidone is used to induce the anisotropic growth and prevent the agglomeration of AgNWs. The polyol synthesis has been conducted by simultaneously injecting the silver precursor in EG and the PVP in EG to a preheated EG solution containing or not a metal salt [15-17]. In this case formation of seeds, nucleation and growth take place simultaneously at high temperatures. In a modified polyol synthesis, the silver precursor in EG, the PVP in EG and $FeCl_3$ in EG were added to an EG solution at room temperature and then heated-up to the reaction temperature [18]. The heat-up process promoted the formation of multiple-twinned Ag seeds and their growth into nanowires presumably because the oxidative etching is not too severe during initial Ag seed formation, since the nucleation occurs at relatively low temperatures.

Metal salts ($PtCl_2$, NaCl, $CuCl_2$) have been sometimes used in a salt-mediated polyol synthesis. The addition of trace amounts of salt has been shown to influence the morphology of the final product. The addition of NaCl in the polyol synthesis leads to the formation of AgCl, thus decreasing the amount of free Ag^+ ions in the solution and hence slowing down the kinetics of the reduction process of $AgNO_3$, enabling the growth of Ag nanoparticles into nanowires [19]. Other studies showed that the molar ratio of NaCl/$AgNO_3$ strongly affects the shape of the final product [20-22]. Thus, in the absence of Cl^- ions mostly spherical Ag particles have been obtained. If the molar ratio is 1, then the Ag^+ ions come from dissociation of AgCl in EG. Because the solubility constant of AgCl in EG is reduced, the concentration of Ag^+ ions is low even at high temperatures and twinning probability is also low, leading preferentially to single crystal cubes and bipyramids. For intermediate values of NaCl/$AgNO_3$ molar ratio, AgCl is formed, but a large excess amount of $AgNO_3$ is also present in the solution. Under such conditions the growth of nanowires is possible.

Here we report a modified polyol synthesis method, where AgCl nanocrystals previously formed in the absence

of the surfactant, by the reaction between silver precursor in EG and ethanolic NaCl solution are used as heterogeneous nucleation seeds for AgNWs. Several synthesis parameters have been varied, such as: injection temperature of AgCl seeds, formation of AgCl seeds in the absence or presence of PVP, PVP/AgNO$_3$ molar ratio and their effect on the geometry and aspect ratio of the synthesized AgNWs has been studied.

2. Experimental

2.1. Synthesis of Ag nanowires

AgNWs have been synthesized through a modified polyol process in the presence of chloride ions, as described in details below [23]. First, 0.3 mmol of AgNO$_3$ was dissolved in 5mL of analytical grade ethylene glycol (EG) and 0.5 mL of 3.9 mM NaCl ethanolic solution was added dropwise under stirring in the dark. The addition of NaCl led to the precipitation of AgCl, thus obtaining a AgCl suspension in EG, which was stirred for 5 min using a magnetic stirrer. Then 0.9 mmol polyvinylpyrrolidone (PVP) (M$_W$ = 40,000) was dissolved in 10 mL EG, the solution was transferred into a Pyrex reactor and degassed by bubbling N$_2$. The solution containing both silver precursor and AgCl clusters was injected at ambient temperature into the reactor containing the PVP solution in EG. The concentrations of AgNO$_3$, NaCl and PVP in the final solution were, respectively, 19.35, 0.125, 58 mM. Then, the reactor was heated in an oil bath with a constant rate of 4°C/min up to 160°C under stirring at 200 rpm and under a nitrogen blanket which was obtained by using the N$_2$ purge system. Stirring of the reaction medium was performed using a magnetic stirrer placed under the oil bath. After reaching 160°C, the mixture has been kept under stirring at this temperature for 1 h, than it has been cooled down by removing the reactor from the heating oil bath.
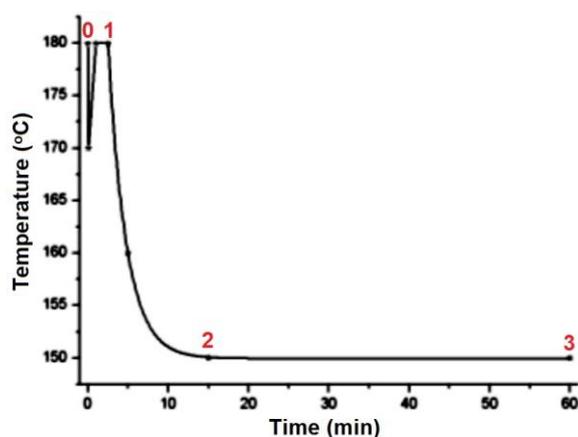
Fig. 1. Thermal regime for the synthesis of samples S20AW(1-3). In points 1, 2 and 3 samples were extracted for TEM and UV-Vis studies

To study the influence of injection temperature, the synthesis has been performed by heating up the PVP solution in EG under N$_2$ bubbling with a constant rate of 10°C/min up to 160°C. Than, the previously formed solution containing both silver precursor and AgCl clusters was injected at different temperatures (80°C, 130°C, 160°C and 180°C) and the reaction mixture is maintained at 160°C for 1h. When the Ag precursor is introduced at 180°C, the temperature falls according to the program shown in Fig. 1 and samples are extracted and analyzed after 3 min, 15 min and 1h.

The PVP/AgNO$_3$ molar ratio was increased to 6 : 1 and the injection temperature of Ag precursor and AgCl clusters was 25°C and respectively 160°C.

An overview of the AgNWs samples and the corresponding synthesis conditions is given in Table 1.

Table 1. Synthesis conditions of AgNWs

Sample	Injection temp. °C	Molar ratio PVP : AgNO$_3$	Synthesis temp. °C
S6AW	25	3 : 1	160
S4AW	80	3 : 1	160
S12AW	130	3 : 1	160
S5AW	160	3 : 1	160
S20AW	180	3 : 1	150
S7AW	25	6 : 1	160
S17AW	160	6 : 1	160
S10AW	160*	3 : 1	160
S13AW	130**	3 : 1	160

*AgNO$_3$ was injected in the PVP/NaCl/EG solution
** PVP was injected after 1 minute in AgNO$_3$/NaCl/EG

In all cases, the purification of AgNWs has been made by extracting the original solvent used in the synthesis by centrifugation at a speed of 4000 rpm and redispersion of the nanowires in ethanol 96%. For samples obtained at higher injection temperature a speed of 10000 rpm was necessary. After three cycles of washing, centrifugation and dispersant replacement, the yield of purified AgNWs was 19%. The nanowires have been redispersed in 5mL ethanol, yielding a slurry with a concentration of 1.2 mg/mL AgNWs.

2.2. Characterization

The obtained silver nanostructures were characterized by multiple methods: X-ray diffraction (X'Pert PRO MPD PANalytical diffractometer, CuKa radiation, λ = 1.54184 Å, Bragg-Bretano geometry, Automatic Divergence Slit, PIXcel detector, UV-Vis spectroscopy (Lambda 950 Perkin-Elmer spectrometer), scanning electron microscopy and EDX elemental analysis (FEI Inspect S), transmission electron microscopy (FEI Tecnai G2).

3. Results and discussion

To study the influence of the injection temperature on the geometry and aspect ratio of the synthesized AgNWs, the soluble silver salt and the AgCl clusters were injected at different temperatures: 25°C (S6AW), 80°C (S4AW), 130°C (S12AW), 160°C (S5AW) and 180°C (S20AW).

As shown in the SEM images (Fig. 2), injection at 25 and 160°C leads to a high amount of silver nanowires in the final product, having diameters around 50 nm. However, the dispersion of diameter values is narrower when injection is performed at 160°C instead of 25°C. The average length of the nanowires obtained by injection of precursor at 160°C is about 5 μm, and by injection at room temperature, it is 3.5 – 4 μm. The difference is due to the fact that, although the density of Ag clusters formed during slow heating of silver precursor is lower than for injection directly at high temperature, the seeds created at lower temperature do not lead exclusively to the formation of nanowires and nanoparticles having other shapes are consuming a part of silver precursor by their growth, limiting the length of obtained AgNWs.
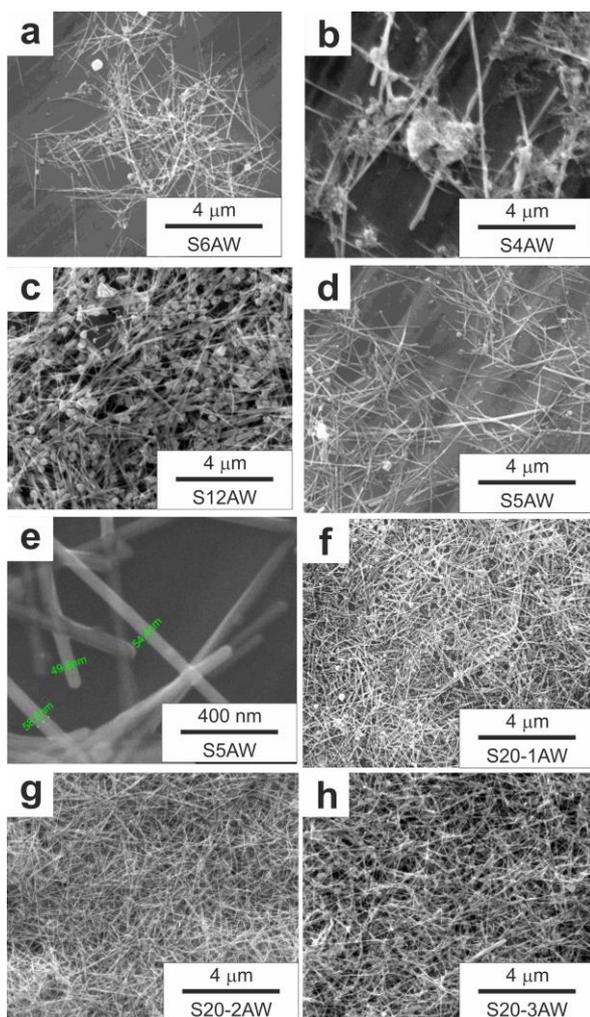
Fig. 2. SEM images of as synthesized AgNWs obtained at different injection temperatures of AgNO$_3$ and AgCl clusters: 25°C (a), 80°C (b), 130°C (c), 160°C (d-e) and 180°C (f-h)

The average diameter of nanowires obtained at 25 and 160°C is about 50 nm, resulting in an average aspect ratio (AR = L/D) of 80 for sample S6AW and over 100 for sample S5AW. At intermediate injection temperatures (80 and 130°C) the final product contains high amounts of quasi-spherical silver nanoparticles. Injection of precursor at 180°C leads to the formation after the first three minutes of reaction of a mixture of silver nanowires and nanoparticles with different shapes, mainly spherical and cubic (Fig. 2f). Further growth of nanowires at 160°C (Fig. 2g and h) leads to the reduction of the amount of nanoparticles but also to an increase of the diameter of nanowires. It has been established that, to obtain a high aspect ratio and a high proportion of nanowires, the optimum temperature for the injection of silver precursor and AgCl clusters is 160°C.

The influence of preparation conditions of AgCl nucleation seeds on the reaction product was determined by obtaining AgCl clusters in the absence or presence of PVP at different temperatures. If the AgCl seeds are formed previously at 25°C in the absence of PVP and then injected to the PVP/EG solution heated at 160°C nanowires are obtained in high proportion. On the contrary, the introduction of silver salt in the PVP and NaCl mixture dissolved in EG and heated up to 160°C leads to inhibition of AgCl crystallization by the surfactant and high temperature and in the absence of AgCl clusters, the final product is strongly different. Although Cl$^-$/Ag$^+$ and PVP/Ag$^+$ molar ratios and injection temperature are identical, the final product contains a mixture of cubes, bipyramids and nanoparticles with very few nanowires (Fig. 3).
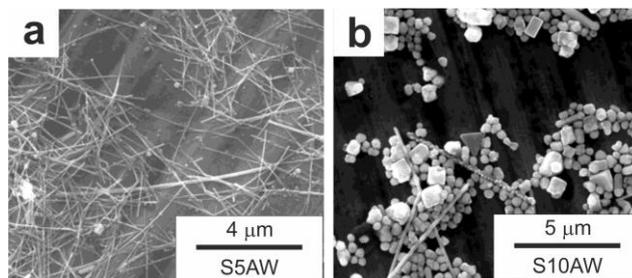
Fig. 3. SEM images of final product obtained by injecting previously formed AgCl clusters at 25°C (a); by forming AgCl clusters in situ at 160°C (b)

The mechanism of AgNWs growth in the presence of Cl$^-$ ions and under bubbling of either N$_2$ or O$_2$ is explained in detail by Tang *et al.* [21]. In the presence of N$_2$ preferably cubes and bipyramids are obtained.

To find out whether AgCl clusters formation is inhibited by surfactant or high temperature, further experiments have been carried out by injecting the silver precursor in the PVP and NaCl mixture dissolved in EG and heated up to 130°C. Thus, the AgCl clusters were formed in situ at 130° in the presence of PVP. In another experiment, the silver precursor was added to a solution of NaCl in EG heated at 130°C. After one minute of injection, the corresponding amount of PVP in EG was

added. Therefore, the AgCl clusters were formed at 130°C in the absence of PVP and in conditions of silver reduction rate much lower than at 160°C. In both experiments the temperature was then increased to 160°C and the remaining operations were identical. The corresponding SEM images of the reaction product are given in Fig. 4. SEM images reveal that in situ formation of AgCl nucleation seeds at 130°C, both in the presence and absence of PVP, leads to a reaction product richer in silver nanowires than in case of AgCl clusters formation at 160°C. Since the solubility of AgCl in EG increases with temperature, more AgCl clusters are available at 130°C for the growth of nanowires. At 160°C the solubility constant of AgCl in EG increases and the rate of AgCl clusters formation is lower than the rate of Ag^+ reduction to Ag, therefore preferably nanocubes and bipyramids are obtained. Also the presence of PVP obstructs the crystallization of AgCl clusters. As a result fewer nanowires are produced when AgCl forms at 130°C in the presence of PVP (Fig. 4).
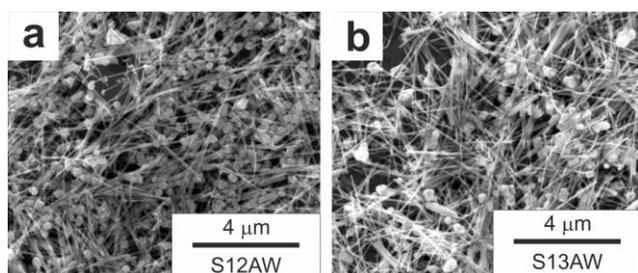
Fig. 4. SEM images of final product obtained by forming AgCl clusters in situ at 130°C in the presence (a) and in the absence of PVP (b)

It has been shown that AgCl nanocrystals can act as heterogeneous nucleation centres for the synthesis of silver nanowires only if the AgCl clusters are produced in the absence of surfactant PVP and at low temperatures.

Doubling the $PVP/AgNO_3$ molar ratio from 3:1 to 6:1 leads to the increase of silver nanowires length to over 10 μm, but at the same time increases the average diameter of the obtained nanowires (see Fig. 5).
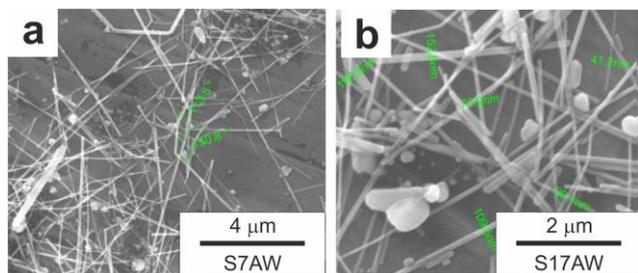
Fig. 5. SEM images of as synthesized AgNWs obtained at $PVP/AgNO_3$ molar ratio of 6:1 and different injection temperatures: 25°C (a) and 160°C (b)

The transmission electron microscopy analysis of samples obtained after 3 minutes of reaction (Fig. 6a) reveals the presence of a mixture of nanorods and various shaped nanoparticles with sizes of 60-70 nm. The high resolution TEM (HR-TEM) image of a single nanoparticle (Fig. 6b) shows a five-twinned decahedral nucleation centre with some structural defects at the twin boundaries due to mechanical stresses. Also, the HR-TEM image of a single nanowire (Fig. 6c) shows two distinct crystalline domains in the same nanowire, which highlights its polycrystalline nature.
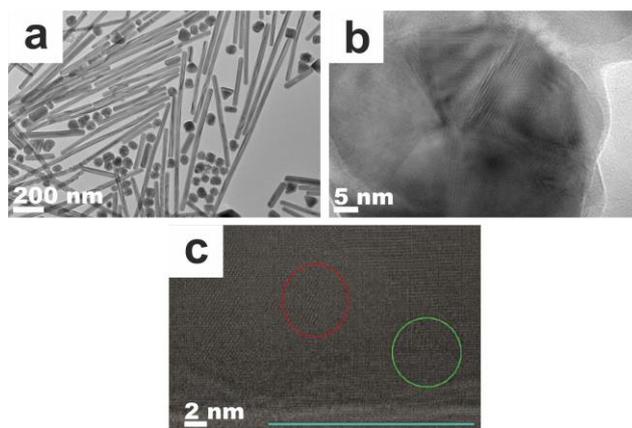
Fig. 6. (a) TEM image of a AgNW sample extracted after 3 minutes of synthesis (S20AW1). (b) HR-TEM image of a single Ag nanoparticle. (c) HR-TEM image of a single nanowire

Fig. 7a gives the X-Ray diffraction patterns for samples mentioned in Table 1. Diffraction peaks of all samples can be assigned to face-centered-cubic phase of Ag (PDF 01-089-3722), grown preferentially along the direction [111], as majority phase. Some samples are slightly contaminated with AgCl. The EDX spectrum of sample S6AW (Fig. 7b) confirms the XRD results by showing the presence, besides Ag, of small amounts of Cl and C (due to PVP).

The morphology of samples containing Ag nanostructures can be also studied by UV-Vis absorption spectroscopy. The surface plasmon resonance (SPR) bands for Ag nanostructures depend strongly on the shape and size of these nanostructures. According to literature, the main SPR peaks for Ag nanorods and nanowires appear at ca. 350 and 380 nm [15,16]. Small size spherical Ag nanoparticles show a peak at ca. 410 nm [13,15,16], while Ag nanoparticles with other shapes exhibit absorption maxima at higher wavelength, around 470 nm for cubic and 520 nm for bipyramidal structures. The absorption spectra are size-dependent, as observed for cubic Ag nanoparticles, when the SPR band shifts from 450 nm to 500 nm as the edge length increases from 30 to 60 nm [24]. When a mixture of Ag nanostructures with various shapes and sizes is obtained, the corresponding peaks overlap.

UV-Vis absorption spectra of samples obtained after various reaction times (3 min, 15 min and 1 h) and also

after purification of samples by centrifugation are given in Fig. 8.

a

b
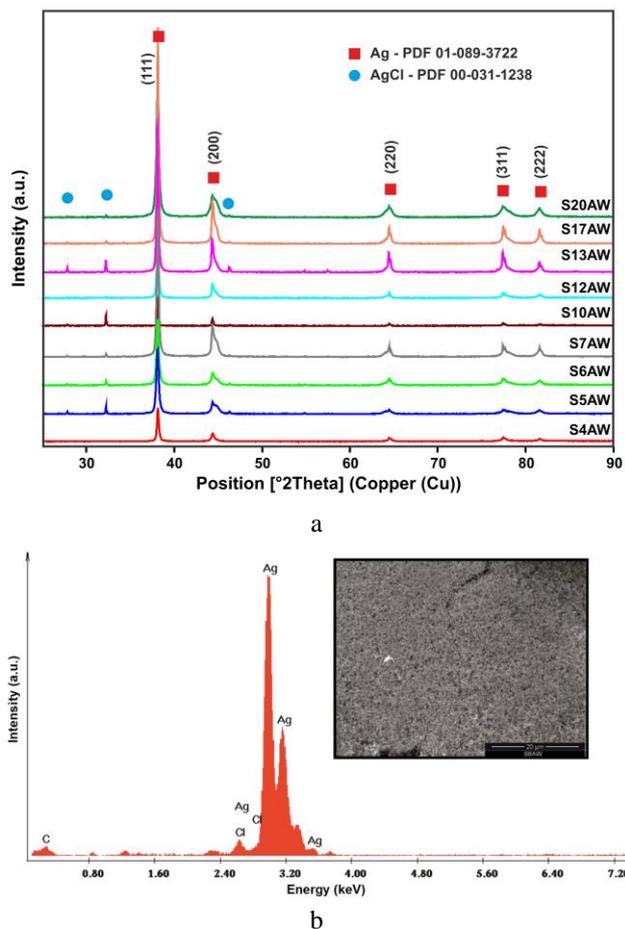
Fig. 7. (a) XRD patterns for as synthesized AgNWs according to Table 1; (b) EDX spectrum of sample S6AW
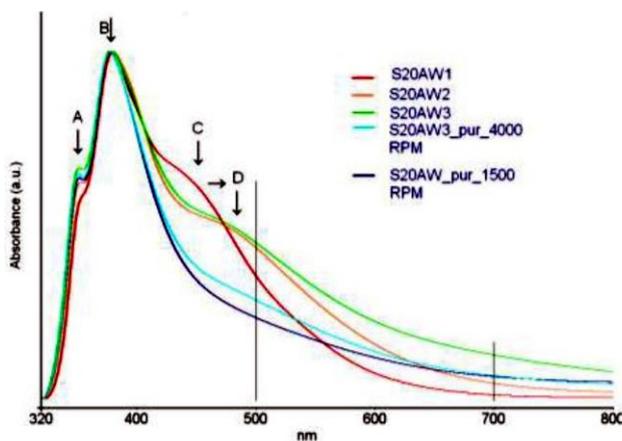
Fig. 8. Normalized UV-Vis absorption spectra of samples obtained after 3 min (S20AW1), 15 min (S20AW2) and 1 h (S20AW3) of reaction and after purification

After 3 minutes of reaction, a strong peak is observed at 378 nm and a shoulder at 350 nm corresponding to SPR bands of 1D Ag nanoparticles. A broad band around 450 nm, which shifts to about 490 nm as the reaction time increases and disappears after purification, is attributed to the superimposed plasmonic absorptions of Ag nanoparticles with various shapes. Also, a slight broadening of the strongest peak, which shows a weak shoulder at 410 nm that disappears after purification, indicates the presence of small quasi-spherical Ag nanoparticles in the final product. The results are in agreement with SEM and TEM observations.

4. Conclusions

We have synthesized silver nanowires by a modified polyol method, in the presence of silver chloride clusters obtained by the reaction between the silver precursor and sodium chloride. It has been shown that AgCl nanocrystals can act as heterogeneous nucleation centres for the synthesis of silver nanowires only if the AgCl clusters are produced in the absence of surfactant PVP and at low temperatures. If the AgCl clusters are obtained in situ at 160°C and in the presence of PVP, the reaction product predominantly contains various shaped nanoparticles. If the AgCl clusters are produced in situ at 130°C, a mixture of silver nanowires and nanoparticles is obtained.

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