

Room temperature synthesis of silver nanowires from tabular silver bromide crystals in the presence of gelatin

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Abstract

Long silver nanowires were synthesized at room temperature by a simple and fast process derived from the development of photographic films. A film consisting of an emulsion of tabular silver bromide grains in gelatin was treated with a photographic developer (4-(methylamino)phenol sulfate (metol), citric acid) in the presence of additional aqueous silver nitrate. The silver nanowires have lengths of more than 50 μm , some even more than 100 μm , and average diameters of about 80 nm. Approximately, 70% of the metallic silver formed in the reduction consists of silver nanowires. Selected area electron diffraction (SAED) results indicate that the silver nanowires grow along the [111] direction. It was found that the presence of gelatin, tabular silver bromide crystals and silver ions in solution are essential for the formation of the silver nanowires. The nanowires appear to originate from the edges of the silver bromide crystals. They were characterized by transmission electron microscopy (TEM), SAED, scanning electron microscopy (SEM), and powder X-ray diffraction (XRD).

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1. Introduction

Highly anisotropic noble metal nanowires have attracted considerable interest due to their potential applications in optical, electronic, and mechanical nanodevices [1–3]. Silver is especially attractive because it exhibits the highest electrical and thermal conductivities among all metals, and it has been used in a wide variety of commercial applications that range from catalysis and electronics to photonics and photography [4]. As a result, the synthesis and characterization of nanostructured silver have recently attracted the interests of numerous research groups [5–10]. The most widely used methods for the preparation of 1-D nanomaterials can be loosely summarized as template-directed syntheses. Generally, a material is deposited into or onto the template to afford the desired shape followed by separation of the nanostructured product from the template. Both “hard” and “soft” materials have been used

as templates [3,11]. Typically, “hard” templates are made of solid materials containing channels, pores, or steps [12]. Examples for “soft” templates include DNA chains [13], peptide nanotubes [14], polyvinylpyrrolidone (PVP) [7], or glycolipid nanotubes [15].

The formation of small silver particles by the reduction of silver salts is the heart of photography [16]. Several years ago, it was reported that the photographic process could also be applied for the preparation of silver nanowires [17]. Typically, the active part of a photographic film consists of a dispersion of silver bromide crystallites in gelatin. Exposure to light generates silver clusters on the surface of the silver bromide crystallites, which serve as seeds for the generation of the large silver particles that make up the image. Usually, these silver particles are assemblies of silver nanofilaments with a structure similar to that of a wad of steel wool [16,18]. It has been shown that variations in the reaction conditions of the reduction of the silver salts, i.e. the development, can lead to different silver nanostructures. For example, thick short silver needles with diameters around 200 nm and lengths of up to 4 μm were

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obtained from octahedral silver bromide grains [19]. Longer silver nanowires (about 9 μm) were prepared from silver bromide nanocrystals, albeit in low yields [17]. Application of a diluted developer resulted in the formation of short thick silver nanofilaments starting from tabular silver bromide crystallites [20]. Several growth mechanisms have been proposed for the formation of the silver filaments, but the details are still not completely understood [16]. For example, neither the role of the gelatin nor the shapes and sizes of the silver bromide crystallites have been included in the proposed mechanisms.

Here we report a simple method for the synthesis of silver nanowires with an average diameter of ca. 80 nm and lengths of several tens of micrometers, some even over 100 μm , in good yields (over 70% by weight). Contrary to the preparation of photographic films [21] the silver bromide emulsions used in this study were neither chemically nor spectrally sensitized, and all experimental procedures could be performed under fluorescent laboratory light rather than in a darkroom. The methodology is derived from the one reported by Liu et al. [17], but this contribution focuses on yield and quality improvement and partial mechanistic understanding.

2. Experimental section

2.1. Starting materials

A cattle bone-type photographic grade gelatin (Bloom 275 g) was a gift from Kodak. Silver nitrate of purity >99.9% was purchased from Alfa Aesar, potassium bromide (AR) from Mallinckrodt. The Kodak developer D-72 and Kodak F-5 fixer were prepared according to literature procedures [22]. Tabular silver bromide crystals were obtained according to modified literature procedures as outlined below. Silver bromide crystal size, shape and dispersity are strongly dependent on the reaction conditions [21,23,24].

2.2. Synthesis of an emulsion of tabular silver bromide and gelatin

Gelatin (0.75 g) was allowed to swell by soaking in distilled water (50 mL) for 30 min at 45 °C. KBr (0.59 g, 5.0 mmol) was added, and the mixture was stirred at 45 °C for 50 min. Solutions of AgNO_3 (10 mL, 2 M) and KBr (10 mL, 2 M) were added dropwise to the gelatin solution at the same rate and time. The resulting emulsion was stirred for 15 min and then cooled to 4 °C overnight. The solidified emulsion was cut into small pieces (0.5 cm in diameter), and the pieces were washed with distilled water six times each to remove dissolved KBr and KNO_3 (i.e. in each wash cycle the pieces were immersed in distilled water (100 mL) for 15 min). Finally, a gelatin solution (10 mL, 7.5% by weight) was added to the emulsion, the mixture was homogenized by stirring at 45 °C for 15 min and cooled to 4 °C in a

refrigerator for storage. Gelatin weight percent: 5.17%, Gelatin:silver ratio = 1:1.39.

2.3. Film preparation

Glass slides or plastic substrates were coated with liquefied (45 °C) AgBr/gelatin emulsion. The films that had been coated onto plastic substrates can be peeled off to afford freestanding films. All samples were prepared not in a darkroom but under the fluorescent light in the laboratory.

2.4. Reducing agent [25]

Solution A: 4-(methylamino)phenol sulfate (metol, 2 g, 5.8 mmol) and citric acid (10 g, 4.7 mmol) were dissolved in water to give 100 mL solution.

Solution B: AgNO_3 in water (10% by weight). Immediately before use, two parts of solution B were added to 100 parts of solution A. Dilute reducing agent: 100 mL 1/2 concentration of solution A and 2 mL 1/10 concentration solution B.

2.5. Development and fixation

The slides or plastic substrates covered with the AgBr/gelatin emulsion were submerged in a solution of the reducing agent, i.e. the developer, for a certain time, followed by submerging in a fixer, and finally washed by submerging in distilled water.

2.6. Replica

The developed AgBr was separated from the bulk gelatin by centrifugation of a dilute sample. The AgBr grains and silver particles or nanowires were then deposited on a cover glass and dried. Shadowing with tungsten was carried out at an angle of 45°, followed by covering with carbon using a JEOL JFB 900. Finally, the carbon replicas, with the silver and silver bromide particles still attached, were released from the cover glass by treatment with dilute hydrofluoric acid and washed with water. The silver bromide was removed by further treatment with sodium thiosulfate solution. After washing, a copper grid was used to fish out the floating samples.

2.7. TEM samples

After development the slides with the films were treated with the Kodak F-5 fixer for 4 min. Parts of the films broke into fragments and floated on top of the fixer solution. These very thin fragments (approximately 250 nm thick) were transferred to distilled water and loaded onto the transmission electron microscopy (TEM) grids after 20 min. Thus, the TEM images show the exact morphology of the products in the film after reduction.

Table 1
Post-fixation results for tabular AgBr samples

Sample/property	Development time (min)	Color of wet sample	Color of dry sample	Shape	Particle size (nm)	Film no.
Ag-48	10	Bright yellow	Pale purple	Sphere	30–50	32821–27
Ag-49	45	Gray green	Gray	Triangle, hexagon	100	32813–20

2.8. Film sections

The dried freestanding AgBr/gelatin film was embedded in resin. After the resin solidified, it was cut into sections with a thickness of approximately 80 nm by microtomy. These sections were put on a Cu TEM grid.

2.9. Characterization

TEM was performed on a JEOL TEM-2000 at 200 kV and scanning electron microscopy (SEM) using a JEOL 880 SEM. X-ray diffraction (XRD) patterns were taken with a SCINTAG XRD Xtra X-ray diffractometer (CuK α , radiation, 20 kV). The coated slides themselves were used for XRD measurements.

2.10. Post-fixation process

The exposed silver bromide was dissolved from the slide before development leaving the silver nanoparticles or clusters in the gelatin layer. This was achieved by immersion of the slides containing the tabular AgBr/gelatin emulsion in 10% Na₂S₂O₃ solution for 4 min followed by washing for three times in distilled water. The development times were varied, and the results are shown in Table 1. To obtain samples for TEM the resulting film was dissolved in 45 °C deionized water. The silver nanoparticles were separated by centrifugation followed by re-suspending in warm water. This process was repeated three times. A few drops of water were added to the silver deposit to produce an aqueous suspension, which was dropped onto the copper grids for TEM analysis.

3. Results and discussion

Gelatin emulsions of tabular silver bromide crystals were prepared according to modified literature procedures [21,23,24]. The SEM image (Fig. 1a) illustrates the typical morphology of the silver bromide crystals, which were obtained as a mixture of triangular and hexagonal plates with an average size of about 1 μ m (edge length) and a thickness of about 100–150 nm. The TEM image of a carbon replica after removal of the silver bromide grains with sodium thiosulfate (Fig. 1b) shows the presence of silver nanoparticles that have been on the surface of the silver bromide crystals. These nanoparticles were generated by exposure of the emulsion to ambient laboratory light.

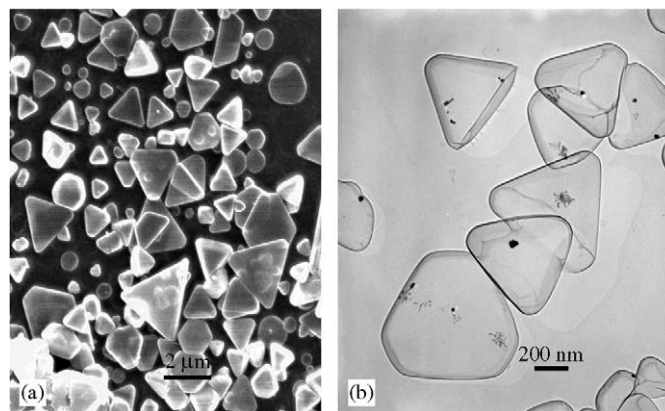


Fig. 1. (a) SEM image of tabular AgBr crystals. (b) TEM image of the carbon replica of tabular AgBr crystals after removal of AgBr with the F-5 fixer.

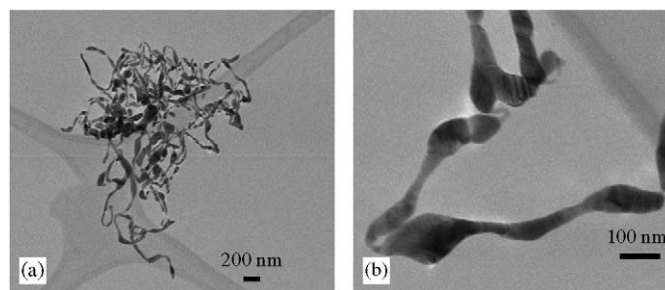


Fig. 2. Silver filaments from development with D-72: (a) 2 min development, (b) 4 min development.

Treatment of these emulsions with different developers under systematically varied reaction conditions afforded silver nanowires and other nanoparticles. The products were generally characterized by TEM and in selected instances also by SEM and powder XRD. For comparison with commercial films, some of the gelatin emulsions were treated with a standard commercial developer, D-72. In this case, tangled and non-uniform nanofilaments were obtained (Fig. 2), which is typical for the form of silver found in photographic films after development [16].

Long silver nanowires were obtained in good yields by application of a mild reducing agent in the presence of silver nitrate. Fig. 3 shows a typical TEM image of these nanowires with diameters in the range of 60–80 nm, and lengths of up to several tens of micrometers with some wires reaching lengths of more than 100 μ m. It should be



Fig. 3. A typical low magnification TEM image of silver nanowires obtained from tabular AgBr crystals after 5 min development.

mentioned that these images reflect exactly how the silver nanostructures existed in the gelatin film, because the TEM samples consisted of the top layer of the gelatin film. Although some silver nanoparticles and short filaments were also found in the products, the nanowires' weight percentage was estimated at more than 70%. This is significantly higher than the 30% reported previously [17]. The TEM image of an individual silver nanowire is shown in Fig. 4. Several selected area electron diffraction (SAED) images taken in different areas of the nanowire suggest that the nanowire is single crystalline cubic silver with a growth direction along the $[111]$ vector.

The penetration depth of the developer was probed by TEM on thin cross-sections of free standing developed gelatin film. Fig. 5 shows that the silver particles and nanowires are concentrated in the top 250–300 nm layer, and none were found deeper than 700 nm. Apparently, the reaction is confined to the surface layer, and this may be explained in two ways: (i) the reducing agents and the Ag^+ ions diffuse only slowly into the gelatin film during the 5 min reaction time or (ii) the Ag^+ ions were consumed while permeating the gelatin film.

In order to gain deeper understanding of the growth mechanism of the silver nanowires, a series of experiments with systematically varied reaction conditions was conducted. Treatment of a gelatin film that did not contain silver bromide with our developer (solutions A and B) led to the deposition of metallic silver on the surface of the gelatin as well as on the wall of the beaker. Only irregularly shaped silver was formed, and no nanowires were detected. Treatment of silver bromide grains in the absence of gelatin under otherwise identical conditions similarly afforded

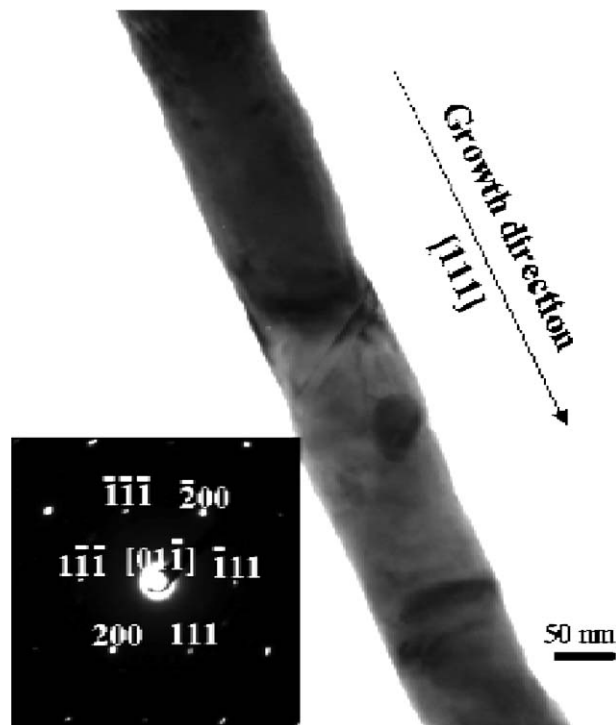


Fig. 4. A close-up image of an individual silver nanowire. The inset shows an electron diffraction pattern from this wire indicating the growth direction as $[111]$.

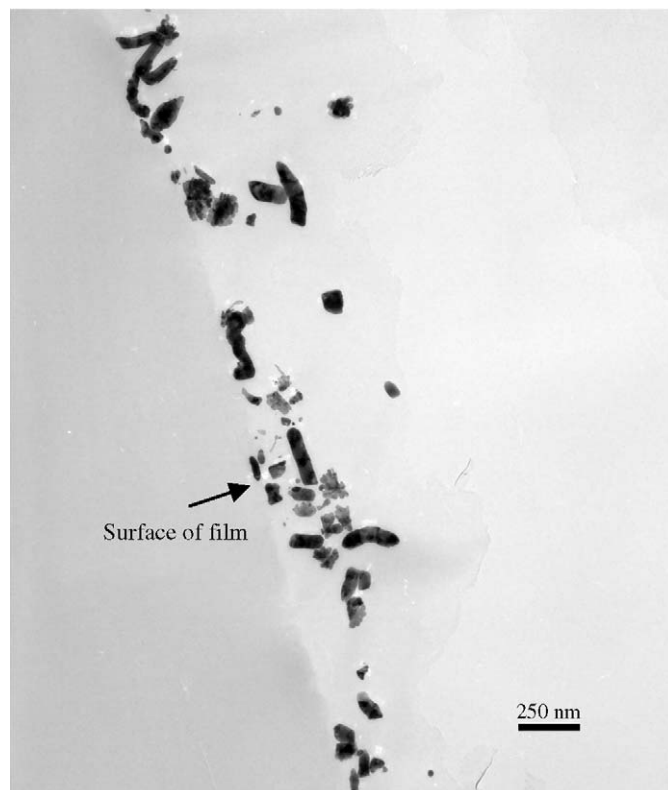


Fig. 5. TEM image of a sectioned sample of silver nanowires inside the gelatin film.

only coarse silver particles. Next, a suspension of silver nanoparticles in gelatin was generated by exposure of the silver bromide/gelatin emulsion to laboratory light followed by removal of the silver bromide with sodium thiosulfate solution (post-fixation process). Under these conditions the silver nanoparticles that have formed on the surface of the silver bromide grains (see Fig. 1b) remain suspended within the gelatin. Treatment of this emulsion with our developer again did not lead to silver nanowires, but instead to formation of various silver particles depending on the reaction time. A brief (10 min) contact with the developer gave oval-shaped silver nanoparticles with an average size of about 30 nm (Fig. 6a). A longer reaction time (45 min) afforded well-shaped hexagonal or truncated trigonal silver prisms with an average size of 100 nm. These particles may be compared with those obtained recently by reduction of AgNO_3 with L-ascorbic acid in the presence of silver seeds and cetyltrimethylammonium bromide [26]. Finally, the development times of the silver bromide/gelatin emulsion were varied, and the products were analyzed by TEM using carbon replicas. As silver halides are sensitive to an electron beam, this technique is commonly used to investigate the morphology of silver halides [23] as well as the growth mechanism of the silver filaments in the photographic process [19]. Silver nanowires at different stages of development were observed. Before reduction, there were some silver nanoparticles on the surfaces of the silver bromide grains, which

were caused by photodecomposition (Fig. 1b). Fig. 7 illustrates the silver nanowires formed at different reducing times. After a 2 min reduction some nanoparticles and short nanowires (nanorods) were obtained (Fig. 7a). These nanorods may be viewed as the initial stage of the nanowire formation. Increase of the contact time to 5 min (Fig. 3) resulted in a mixture of nanoparticles and nanowires, with the nanowires already comprising more than 50% of the silver. A high ratio of long nanowires to nanoparticles was observed after 10 min reduction time (Fig. 7b), which did not change significantly using a 20 min development (Fig. 7c). The silver nanowires routinely grew to tens of micrometers in length, some to even more than 100 μm . In most cases, it can be seen that the nanowires originate from the edges or sides of the tabular silver bromide grains. Since the silver bromide crystals remain intact during development, the silver source is most likely the silver nitrate solution that is part of the developer, a process that is known in photography as physical development [16].

The XRD patterns taken from the film samples show that the silver nanowires and silver nanofilaments synthesized here existed solely in the fcc phase (Fig. 8). The lattice constant of the silver nanowires calculated from the XRD pattern was 4.081 Å, which is very close to the reported data ($a = 4.0862$ Å, JCPDS File 4-0783). It is noteworthy that the peak width for silver nanowires (Fig. 8b) is slightly

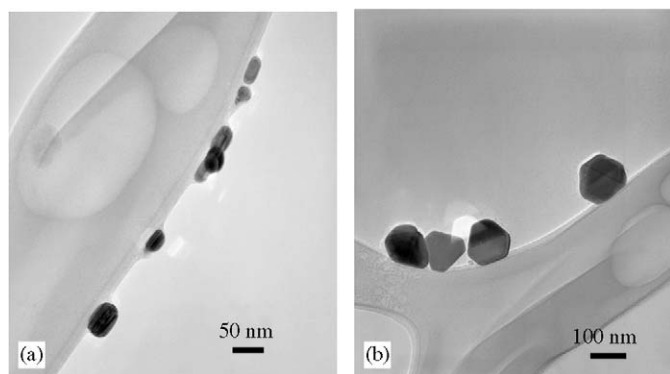


Fig. 6. TEM images of post-fixation samples developed for (a) 10 min and (b) 45 min using diluted developer.

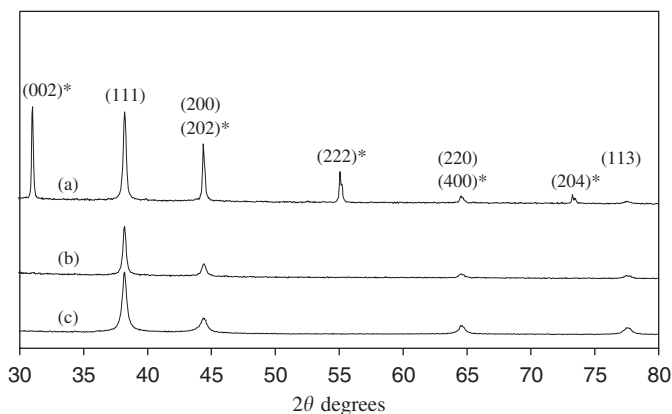


Fig. 8. Powder XRD patterns for (a) silver nanowires before removal of AgBr, (b) silver nanowires and (c) silver nanofilaments. AgBr reflections are indexed with*.

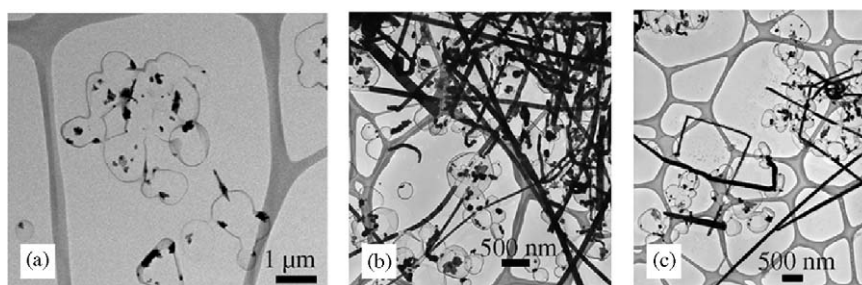


Fig. 7. TEM images of the silver nanowires at different stages of development: (a) after 2 min development, (b) after 10 min development, (c) after 20 min development.

narrower than that for silver nanofilaments (Fig. 8a), indicating a larger average crystallite size of the nanowires [27]. This is consistent with the TEM results, which have shown that the silver nanowires are thicker than the nanofilaments.

The mechanism of the silver nanowire formation is not yet completely understood. However, it has now been demonstrated that the necessary requirements are at least (i) a film consisting of an emulsion of tabular silver bromide in gelatin, (ii) a mild reducing agent, and (iii) the presence of silver ions in solutions. Lack of any of these ingredients does not afford any nanowires. It is interesting to note that the small silver nanoparticles on the surface of the silver bromide crystals apparently do not act as seeds for the silver nanowire growth. On the other hand, it is common in photographic films that silver nanofilaments originate at the edges of the silver bromide grains, although the reason is not clear [20]. The developer is mild enough not to quickly reduce the crystalline silver bromide but mainly the silver ions in solution. It has been suggested that this process may be facilitated by the silver bromide [20]. Silver ions at an edge of a silver bromide grain are reduced, and the silver ions in the grain are replenished by silver ions from the solution. This could account for the here observed nanowire formation. Although the role of gelatin is not yet understood, it may be speculated that it serves a similar role as PVP in that it binds preferably to certain crystal faces [7]. Furthermore, gelatin may also control the diffusion of developer and silver ions and thus limit the concentration of silver ions at the growing structure. Silver has been shown to have an affinity for arginine, cysteine, lysine and methionine [28], and these are also common in gelatin [16].

4. Summary

A fast and facile procedure for the preparation of long silver nanowires was found in the reduction of aqueous silver ions inside a film consisting of a silver bromide/gelatin emulsion in a procedure similar to the development of photographic films. The reaction is fast (10–15 min), proceeds at room temperature on the laboratory desktop under ambient light and affords straight nanowires in high yields. Investigations of the mechanism as well as attempts to increase the yield and selectivity are under way.

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