Synthesis and Characterization of Silver Halide Nanowires[#]

Ran Liu, Flory Wong[†], Wentao Duan[†], and Ayusman Sen^{*}

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, 16802 (USA)

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ABSTRACT: This paper describes a template-assisted synthesis of silver halide nanowires by anodization of silver nanowires in hydrohalic acid solution within an alumina template. The length of the silver halide nanowires was controlled by the charge passed during the anodization process. The silver halide nanowires were characterized using SEM and EDS to determine structural differences, electron beam sensitivity, Ag:X ratios, and other. The template-assisted synthesis is superior to traditional solution-based methods due to the uniformity and controlled shape of the silver halide nanowire product.

1. Introduction

Silver halide nanomaterials [e.g. silver chloride (AgCl) and silver bromide (AgBr) nanoparticles,¹⁻⁵ nanowires^{5,6}] or heterogeneous silver halide nanostructures^{3,6-14} (e.g., core-shell Ag/AgCl nanowires,³ AgCl nanowires decorated with Au nanoparticles,^{15,16} AgBr/polymer composite nanoparticle¹¹) have been synthesized and investigated due to their photocatalytic^{3,6,7,9,10} and antibacterial properties.¹¹ Micron-sized AgCl particles have also been studied by our group as light-powered motors in water.^{16,17} Different approaches have been reported for the synthesis these silver halide nanostructures. For example, Ag nanowires can be converted to Ag/AgCl core-shell nanowires^{3,15} after treatment with FeCl₃. When silver nitrate (AgNO₃) and potassium chloride (KCl) react with the assistance of reserve micelles as the soft template, AgCl/AgBr nanoparticles^{1,4} can be fabricated. In this paper, we present a method to synthesize pure silver halide nanowires based on anodization of silver nanowires in diluted hydrohalic acid solutions with the assistance of an alumina template.

2. Experimental

2.1. Chemicals and Materials

Silver chloride, sodium thiosulfate, potassium metabisulfite, hydrogen chloride, and hydrogen bromide, were purchased from Sigma Aldrich. Silicon wafer (5 mΩ-cm, p-type, 100 crystal orientation) was purchased from Silicon Quest. Alumina template with 200 nm pore size was commercially available from Whatman. Carbon film supported nickel TEM grids (200 mesh) were purchased from Electron Microscope Sciences. Deionized water was obtained using a

[#]Dedicated to John Bercaw, friend and mentor, on the occasion of his 70th birthday.

^{*}Corresponding author. Tel.: +1-814-863-2460; Fax: +1-814-865-5235; Email: asen@psu.edu

Barnstead Nanopure Diamond Water system. All chemicals were used as received and all the solutions were freshly prepared.

2.2. Silver Nanowire Fabrication

Alumina template was sputtered with silver (200 nm) using Kurt Lesker CM-18/RF sputtering system. Silver nanowires were synthesized galvanostatically (-1 mA/cm^2) in the silver sputtered alumina template from a solution consisting of silver chloride (50 g/L), sodium thiosulfate (500 mg/L) and potassium metabisulfite (30 g/L) on the SP-150 potentiostat from Bio-logic. Typical silver nanowire depositions were allowed to proceed for 10 min. All potentials were measured relative to an Ag/AgCl reference electrode using a platinum foil as a counter electrode, if not specified otherwise.

2.3. Template-assisted Halide Anodization

The silver nanowires were anodized by 0.2 M HCl/HBr to form the corresponding silver halide nanowires under the constant current of 0.3 mA/cm^2 at different charge densities. The back sputtered silver and the remaining silver nanowires were etched by 3 M nitric acid (HNO_3) solution for 20 min. The alumina template was subsequently removed by 10% HF solution to release the silver halide nanowires. Released nanowires were centrifuged and washed by deionized water at least 8 times and finally dispersed in deionized water.

2.4. Characterization

Scanning electron microscopy (SEM) images were obtained using the Leo 1530 field emission scanning electron microscope at 3 kV. All the samples were dispersed and dried on the silicon wafer before SEM observation. Energy-dispersive X-ray spectroscopy (EDS) data were collected by JEOL 2010F Field Emission TEM/STEM with EELS and EDS at 200 kV. Electropotential data were obtained via a SP-150 potentiostat from Bio-logic

3. Results and Discussions

3.1. Synthesis

Scheme 1 illustrates the fabrication process for the silver halide nanowires. First, silver nanowires were electrodeposited into the silver sputtered alumina template from a silver deposition mixture containing silver chloride, sodium thiosulfate, and potassium metabisulfite. In this solution, silver chloride slowly dissolves in thiosulfate to form silver thiosulfate (eq. 1).

Potassium metabisulfite was added as the antioxidant. The silver nanowires were then anodized using hydrohalic acid solutions (HX, X = Cl, Br). The process begins on the surface of the silver and proceeds down the length of the wire. Hence, by applying a constant current density of 0.3 mA/cm^2 for 2-20 min, the desired AgX nanowire length can be achieved. Scheme 1d shows the detailed anodization mechanism: Initially the silver metal is oxidized into silver ions (Ag^+),

which diffuse away from the silver surface and meet the halide ions (X^-) to form the silver halide (AgX) layer. Interestingly, even after the AgX layer builds up, the X^- can still penetrate through the initial AgX layer and combine with Ag^+ to form a new AgX layer at the bottom of the existing AgX layer, maintaining continuous growth. This penetration process is probably due to the porosity of the AgX layer. After the AgX was formed on the top of silver nanowires, the remaining silver bottom was etched by 3 M HNO_3 . And the alumina template was finally dissolved by 10% HF to release the AgX nanowires ($NaOH$ was avoided because it can convert the AgX into $AgOH/Ag_2O$).

Scheme 1. Synthesis steps for AgX nanowires ($X=Cl, Br$)

3.2 Material Characterization

Fig. 1. a) Photographs of freshly prepared $AgCl$ and $AgBr$ nanowires dispersed in water. b) Corresponding anodization potentials (vs. $Ag/AgCl$) of Ag nanowires for conversions into $AgCl$ and $AgBr$ at current density of 0.3 mA/cm^2 in 0.2 M HCl or HBr for 20 min.

Figure 1a shows the photographs of AgCl and AgBr nanowires dispersed in water. As can be expected, the colors of these nanowires solution range from white to pale yellow, reflecting the coloration of their respective bulk silver halide compound. Figure 1b displays the potential versus time profiles for silver nanowire anodization. These potential values fit quite well with the theoretical values for Ag/AgX oxidation potentials (eq. 2-3):

The anodization potential for Ag to AgCl conversion kept rising, possibly due to the lower porosity of AgCl that hinders the Cl^- penetration into the AgCl layer.

Fig. 2. a) SEM image of AgCl nanowires, b) EDS analysis of the AgCl nanowires. AgCl nanowires were synthesized by anodizing Ag nanowires at current density of 0.3 mA/cm^2 for 10 min in 0.2 M HCl.

Figure 2 exhibits the SEM image of AgCl nanowires. As can be seen, the surfaces of these AgCl nanowires are quite smooth. EDS elemental analysis reveals that the atomic ratio of Ag to Cl is 1.1:1, which is slightly over 1 due to the AgCl decomposition to Ag under electron beam. The corresponding ratio for AgBr could not be obtained due to the high sensitivity of the material to the electron beam. Figure 3a-3d shows SEM images of AgBr nanowires synthesized via anodization. The images were of the same region after electron beam irradiation at different times. A hole was burned through the bundle after 1-2 min of irradiation, demonstrating the difficulty in obtaining accurate data for Ag: Br ratio.

Fig. 3. a) SEM images of AgBr nanowires synthesized by anodizing the silver nanowires in 0.2 M HBr solution under the current density of 0.3 mA/cm^2 for 10 min, b-d) SEM of same patch of AgBr after electron beam irradiation over time.

When the AgX nanowire surfaces were exposed to the SEM beam, they all started to decompose (Figure 4). As shown in Figure 4c and 4d, silver nanoparticles grow on the AgCl nanowires surfaces under irradiation. Interestingly, these silver nanoparticles tend to grow in lines, probably at the edges of AgCl crystals. We found that this phenomenon is especially evident when the AgCl was synthesized under higher anodization current because materials electro-synthesized at the higher current usually possess larger crystal domains.¹⁸ This was also observed to some extent on AgBr samples (see figure 3).

Fig. 4. a) Schematic of AgCl nanowire before and b) after electron beam irradiation. c) and d) SEM of AgCl nanowires after exposure to electron beam for different times. AgCl nanowires were synthesized by anodizing Ag nanowires at current density of 0.3 mA/cm^2 for 10 min in 0.2 M HCl. (Scale bar = $1 \text{ }\mu\text{m}$)

3.3. Advantages of Template-assisted synthesis

The synthetic approach described in this paper offers two advantages over traditional solution-based methods in generating nanowires. First, when silver is converted to silver halide, the volume of the material is expected to increase. Based on the molecular weight and mass density of AgX and Ag, we can calculate the volume ratios of AgX/Ag to be $V_{\text{AgBr/Ag}} = 2.83$, $V_{\text{AgCl/Ag}} = 2.52$. Such a volume expansion typically causes nanowires to swell and deform. The use of

alumina template solves this problem since the nanowires are constrained by the channels. To demonstrate this, bare silver nanowires were treated with iron chloride (FeCl_3) (see Figure 5). The resulting AgCl nanowires, as expected, were composed of big chunks of AgCl nanoparticles instead of having smooth rod-like surfaces. As can be seen in Figure 2a, AgCl nanowires synthesized using the template-assisted method have a smooth, uniform surface. Alternatively, electrodeposited silver nanowires were anodized without the protection of the template in the presence of HCl. To accomplish this, silver nanowires were electrodeposited into the alumina template, which was subsequently removed before anodization. The nanowire array was then anodized via the experimental procedure described. This resulted in random growth of AgCl nanoparticles around the silver nanowires instead of the formation of pure AgCl nanorods. Some cubic-shaped AgCl nanocrystals were identified, shown circled in figure 6.

Fig. 5. (a) and (c) Silver nanowires before FeCl_3 treatment (b) and (d) after FeCl_3 treatment (5 mM) for 3 min. Silver nanowires are electrodeposited at the current density of -1 mA/cm^2 for 2 min. (Scale bar = $1 \mu\text{m}$)

Fig. 6. Silver nanowires (synthesized under current density of -1 mA/cm^2 for 10 min) were anodized in 0.2 M HCl solution (0.3 mA/cm^2 for 5 min) after removal of alumina template, showing cubic AgCl nanocrystals.

Another reason why template-assisted anodization of Ag to AgX is useful in fabricating uniform AgX nanowires is the control over the length of the AgX nanowires. Faraday's law of electrolysis states that the amount of material deposited in an electrolytic cell is proportional to the total charge passed. Therefore, the length of the Ag nanowire deposited can be easily controlled. The conversion of Ag nanowires into the corresponding AgX nanowires is performed by a second electrochemical reaction also governed by Faraday's law. This allows us to use the

following equation to estimate the length of AgX nanowires synthesized from the anodization process based on the amount of charge passed (see Figure 7):

$$L = M_{AgX} \frac{Q}{F A \rho_{AgX}} \quad (4)$$

where L is the length of AgX nanowire, Q is the charge passed, ρ_{AgX} and M_{AgX} are the density and molecular weight of the AgX, respectively, A is the cross-sectional area, and F is the Faraday constant.

Based on this equation, we can estimate the length of AgBr nanowire should be around 6 micron after 200 mC/cm² charge is passed. However, based on the SEM analysis (Figure 7c), the AgBr nanowire length was only ~3 micron. This suggests that the current efficiency of this electrochemical anodization is only around 50%. The deposition and anodization length for AgCl shows a similar trend.

Fig. 7. AgBr nanowire length vs. charge density for the anodization (a-c). Ag nanowires were anodized in 0.2 M HBr solution under a current density of 0.3 mA/cm².

4. Conclusion

In conclusion, we have described a synthetic approach to silver halide nanowires by anodization of silver nanowires in hydrohalic acid solution within the alumina template. The length of the silver halide nanowires can be controlled relatively easily by varying the charge passed for the anodization process. Synthesized silver halide nanowires were subject to decomposition under the electron beam, resulting in the growth of silver nanoparticles on the surface. In principle, the method presented in this paper can be extended to the synthesis other insoluble metal salt nanowires. Preliminary studies show success in applying this synthetic approach to the fabrication silver iodide nanowires. The method also allows the generation of uniform, photoactive silver halide nanowires that may be used to fabricate light-powered nanomotors.

Author Information

Corresponding author.

Ayusman Sen

Tel.: +1-814-863-2460

Fax: +1-814-865-5235

Email: asen@psu.edu

Author Contributions.

[†]FW and WD contributed equally to this work.

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