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Synthesis and characterization of silver halide nanowires

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

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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 nanoparticle [11]) 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 of these silver halide nanostructures. For example, Ag nanowires can be converted to Ag/AgCl core–shell nanowires [3,15] after treatment with $FeCl_3$. When silver nitrate ($AgNO_3$) 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 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 g/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.

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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.

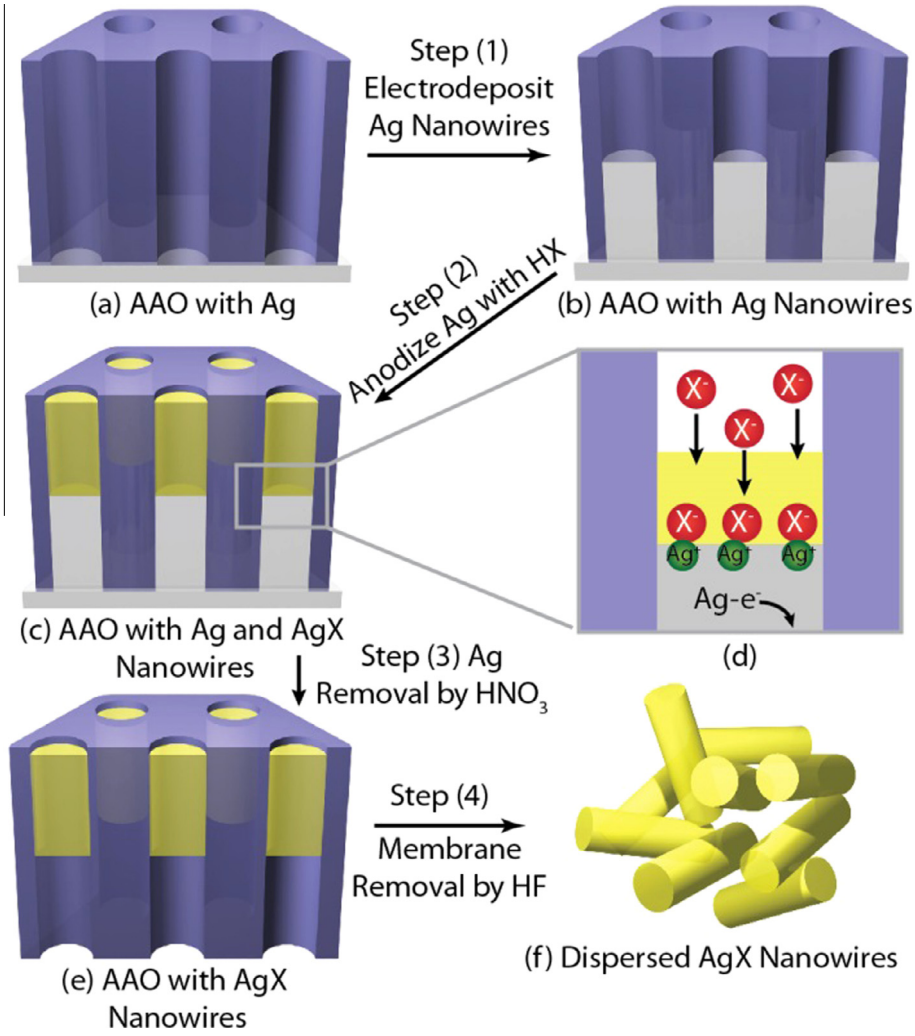
3. Results and discussions

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)).

$$2S_2O_3^{2-} + AgCl \rightarrow [Ag(S_2O_3)_2]^{3-} + Cl^- \quad (1)$$

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).