



Templated electrodeposition of $\text{Ag}_7\text{NO}_{11}$ nanowires with very high oxidation states of silver

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ABSTRACT

The templated electrodeposition of 200 nm diameter nanowires of the argentic oxynitrate $\text{Ag}(\text{Ag}_3\text{O}_4)_2\text{NO}_3$ phase is reported. Their high surface-to-volume ratio and the high average oxidation state of Ag make these wires promising candidates for nanoscale redox processes in which both a high volumetric charge density and a high discharge rate are required. The antibiotic activity of these nanowires was demonstrated by inhibiting the growth of *Bacillus cereus* bacteria.

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1. Introduction

Multifunctional nanowires, sometimes referred to as striped nanowires, have a high potential for use in a wide range of biomedical and nanotechnological applications [1–4]. They can be synthesized by bottom-up approaches that usually employ a templated deposition method. A wide variety of metals, polymers and metal oxide segments can easily be incorporated sequentially into the wires, for instance via templated electrodeposition [5–7]. This permits a high degree of control over chemistry and dimensionality, and yields radially and/or axially segmented nanowires. The modular approach allows the versatile and flexible fabrication of multifunctional nanostructures with multiple elements, each with their own specific function. Multicomponent nanowires could be utilized in applications ranging from sensing, multiplexing, and imaging, to gene delivery and vaccinations. There are also potential applications in which metal or metal-containing composite nanowires can replace more conventional devices, like in micro-electronic circuits or magnetic memories.

Various nanowire components with functional properties have already been reported, e.g., optically active ZnO [6,7], catalysts such as Au and Pt [8], and magnetically active Fe_2O_3 and Fe_3O_4 phases [9]. In this report we extend the templated electrodeposition method to the fabrication of nanowires of the highly oxidative $\text{Ag}_7\text{NO}_{11}$ phase. Studies on this material are relatively scarce [10–13]. The ‘building blocks’ of the

crystal are Ag_6O_8 cages which contain an anion in their centers; NO_3^- in the present case. These cages are connected with AgO_4 units forming the surfaces of the Ag_6O_8 cages. The Ag_6O_8 cages force Ag atoms to realize high valence states that are seldom seen in silver. Ag^{2+} and even Ag^{3+} are present in the crystal structure. Each silver atom in an Ag_6O_8 cage has an average 2.67|e| net positive charge. The silver oxysalt formula is therefore also written as $\text{Ag}^+[(\text{Ag}^{2+})_2(\text{Ag}^{3+})_4\text{O}_8](\text{NO}_3^-)$ or $(\text{Ag}_6\text{O}_8)\text{AgNO}_3$. It has a cubic unit cell ($a=9.890$ Å, $Z=4$, space group $Fm\bar{3}m$) and 4 Ag^+ , 8 Ag^{2+} and 16 Ag^{3+} ions are present per unit cell. The material is superconductive below 1.04 K [14], and has antibacterial and antifungal properties [15]. The gravimetric capacity is very large, i.e., ~480 mAh/g, while the potential discharge rate of the material is very high due to the high redox potentials of Ag^{2+} , Ag^{3+} and Ag^+ . In comparison, the gravimetric capacity of the LiCoO_2 cathode of a lithium ion battery is about 140 mAh/g [16].

2. Experimental

Templated electrodeposition was used for silver oxysalt ($\text{Ag}_7\text{NO}_{11}$) deposition. As a template, commercially available Nuclepore® (Whatman Inc.) polycarbonate track-etched membranes were used. The membrane pore diameter is 200 nm and the pore density is $\sim 3 \times 10^8$ pores/cm². Prior to deposition, a gold layer with a thickness of ~250 nm was sputtered on one side of the membrane using a Perkin-Elmer 2400 sputtering system. After sputtering, the gold coated side of the membrane was attached to a glass slide with double-sided tape. Two of these membrane/glass combinations were used as cathode and anode in a 3-electrode setup using a Bank Elektronik POS 73 potentiostat. The reference potential was set by a 3 M KCl Ag/AgCl reference electrode (REF 321, Radio Analytical).

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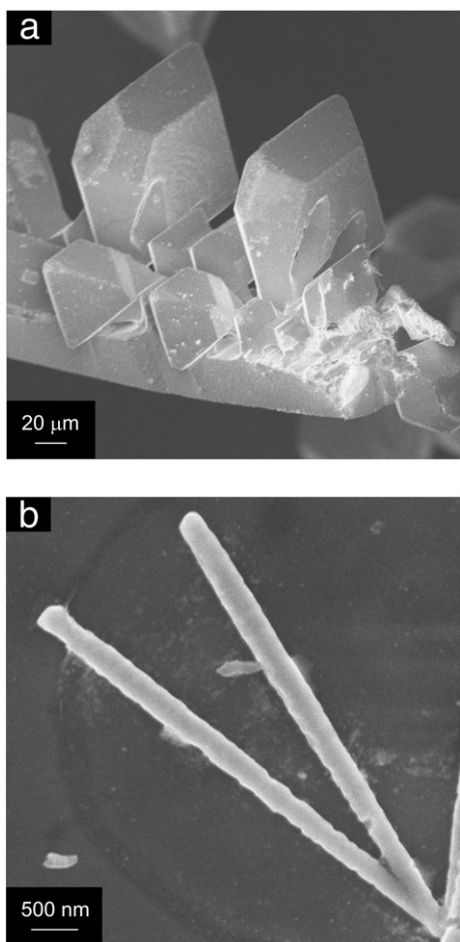


Fig. 1. SEM images of a) a large Ag₇NO₁₁ crystal grown on a Pt electrode; b) two Ag₇NO₁₁ nanowires grown in a PCTE membrane with 200 nm diameter pores.

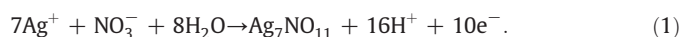
Ag₇NO₁₁ nanowires were deposited from an aqueous electrolyte solution containing 0.2 M AgNO₃ and 0.1 M H₃BO₃. The pH was adjusted to 1.5 with HNO₃. The voltage was set to 1.7 V versus the reference electrode.

Analysis of Ag₇NO₁₁ crystals was performed with a Nikon 600 optical microscope. Analysis of isolated Ag₇NO₁₁ nanowires was performed with a Zeiss HR-LEO 1550 FEF Scanning Electron Microscope (SEM). X-ray diffraction (XRD) was performed with a Philips PanAnalytical PW1830 with a copper X-ray source and a wavelength of 1.54 Å.

The antibacterial activity of the Ag₇NO₁₁ nanowires was demonstrated using an antibiotic sensitivity demonstration kit (Carolina Biological Supply Company, Burlington, North Carolina, US). *Bacillus cereus* (*B. cereus*) bacteria were mixed with molten agar and distributed in a sterile petri dish. Papers infiltrated with Ag₇NO₁₁ nanowires, three different antibiotic disks (Penicillin, Ampicillin and Streptomycin) and a reference paper were placed on top of the agar-*B. cereus* mixture. The petri dish was kept at room temperature in a sterile fume hood for 64 h allowing the bacteria to grow.

3. Results and discussion

Silver oxysalt crystals are normally grown by anodically polarizing a platinum electrode in an aqueous solution of AgNO₃ in a 3-electrode setup [17]. The half reaction at the anode, with a standard potential of +1.59 V versus standard hydrogen electrode (SHE) is [18]



Reduction of Ag⁺ to metallic Ag⁰ occurs at the cathode when it is placed in the same aqueous solution. Without spatial restrictions, argentic oxysalt typically grows as dark gray cubo-octahedral crystals. An example of a large crystal grown on a flat Pt anode is shown in Fig. 1a. These crystals reached dimensions of ~3 cm. To grow nanowires, the platinum anode was replaced by a polycarbonate track-etched (PCTE) membrane with a gold back electrode. The membrane pore diameter was 200 nm and the pore number density is ~3 × 10⁸ cm⁻². The nanowires were deposited from an aqueous solution containing 0.2 M AgNO₃ and 0.1 M H₃BO₃. The pH was adjusted to 1.5 with HNO₃. The voltage was set to +1.7 V versus the Ag/AgCl reference electrode. Fig. 1b shows a Scanning Electron Microscopy (SEM) image of two Ag₇NO₁₁ nanowires grown in this manner.

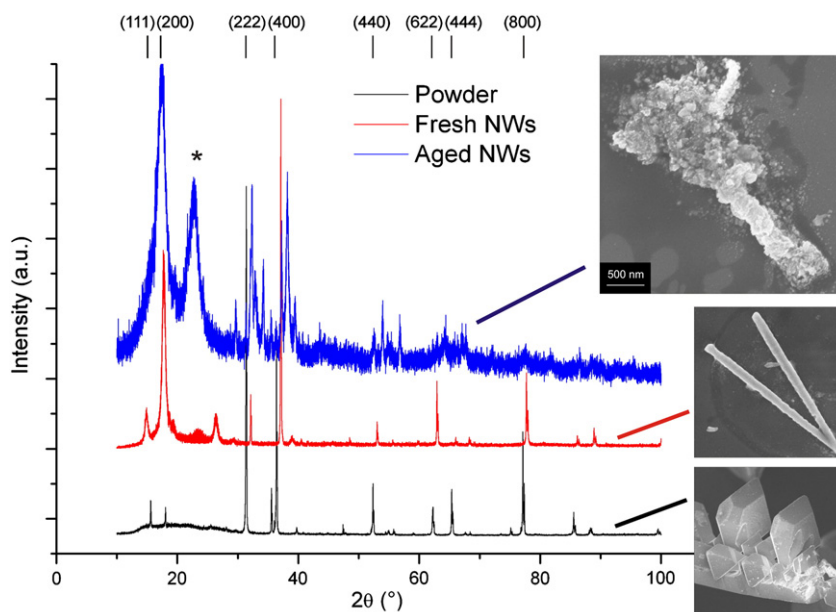


Fig. 2. X-ray diffraction pattern of Ag₇NO₁₁ powder (black), freshly prepared Ag₇NO₁₁ nanowires in a track-etched polycarbonate membrane (red), and Ag₇NO₁₁ nanowires in a track-etched polycarbonate membrane after 1 year storage in air (blue). The asterisk indicates the (101) peak of AgNO₃. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

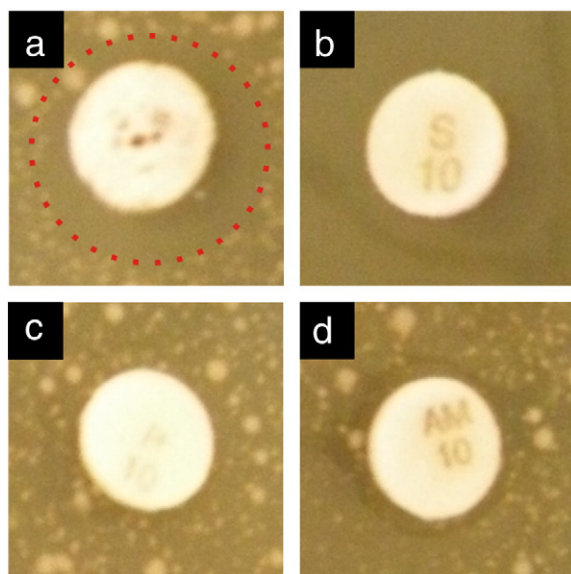
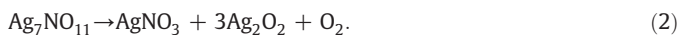


Fig. 3. Selected area photographs of a petri dish containing *B. cereus* bacteria with a) a nanowire-filled paper; b) a paper with Streptomycin antibiotics; c) a paper with Penicillin antibiotics; and d) a paper with Ampicillin antibiotics after growth of the bacteria for 64 h. The inhibition area formed in (a) is indicated with a red circle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The grown nanowires were 200 nm in diameter. To determine the influence of the confined space of the PCTE membrane pores on the predominant growth direction of $\text{Ag}_7\text{NO}_{11}$ nanowires, X-ray diffraction (XRD) spectra of powder and aligned wires were recorded. Fig. 2 shows 2θ scans of a non-oriented silver oxysalt powder of crystals that had been grinded after their growth on a Pt electrode, and a system of as-synthesized nanowires that was still embedded inside a PCTE membrane. Comparison of the two diffractograms shows that the preferential growth direction of silver oxysalt in 200 nm PCTE membrane pores is the (100) direction.

Known solvents for $\text{Ag}_7\text{NO}_{11}$ are ammonium hydroxide and nitric acid [19]. $\text{Ag}_7\text{NO}_{11}$ is known to decompose spontaneously in air over the course of weeks, and at elevated temperatures, like in hot water, in much less time. It then loses molecular oxygen from its crystal lattice, forming silver nitrate and Ag_2O_2 following the reaction



Ag_2O_2 (Ag(I)Ag(III)O_2) has been reported as a grayish black powder. It releases oxygen at temperatures above 100 °C and leaves a residue of metallic silver.

As can be seen in the XRD pattern of the aged nanowires (blue) in Fig. 2, the $\text{Ag}_7\text{NO}_{11}$ phase is still present, but the broadened peaks indicate that the average grain size decreased substantially, which suggests fragmentation of the wires. This was confirmed by the SEM image of aged nanowires in the inset in Fig. 2. Moreover, a strong peak appeared at 2θ 22.8°, which can be assigned to the (101) reflection of AgNO_3 . The formation of silver nitrate is in agreement with the decomposition of $\text{Ag}_7\text{NO}_{11}$ following reaction (2). The silver oxysalt phase could be protected from air by shielding the nanowires and

crystals by coating them with a thin protective gold layer. A galvanic replacement reaction with chloroauric acid (HAuCl_4) was therefore carried out. The $\text{Ag}_7\text{NO}_{11}$ nanowires were placed in an aqueous 5 mM HAuCl_4 solution for 12 h or more. After isolating the crystals from the solution, they had a gold luster (not shown), indicating that the galvanic replacement reaction had taken place.

The antibacterial properties of $\text{Ag}_7\text{NO}_{11}$ nanowires were investigated using *B. cereus* bacteria. Fig. 3 shows selected areas in a petri dish containing *B. cereus* after growth of the bacteria for 64 h at room temperature. An inhibition area without bacterial growth was formed around the nanowire-filled paper and around the paper with Streptomycin antibiotics, but not around the samples with Penicillin and Ampicillin antibiotics. This proves that silver oxysalt nanowires are able to prevent *B. cereus* bacteria from growing and with enough silver oxysalt nanowires, an inhibition area can be observed.

4. Conclusions

$\text{Ag}_7\text{NO}_{11}$ nanowires were synthesized by electrodeposition. The nanowires showed preferential growth in the (100) direction as a result of the spatial confinement of the membrane pores. The sensitivity of $\text{Ag}_7\text{NO}_{11}$ nanowires to air and moisture can be circumvented by coating the crystals with a gold layer via a galvanic replacement reaction. The $\text{Ag}_7\text{NO}_{11}$ phase shows antibacterial activity against *B. cereus*, which is attributed to the high oxidation state of silver ions in silver oxysalts, and the very high surface-to-volume ratio of the nanowires.

Acknowledgment

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