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Field effect transistors based on semiconductive microbially synthesized chalcogenide nanofibers

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ABSTRACT

Microbial redox activity offers a potentially transformative approach to the low-temperature synthesis of nanostructured inorganic materials. Diverse strains of the dissimilatory metal-reducing bacteria *Shewanella* are known to produce photoactive filamentous arsenic sulfide nanomaterials by reducing arsenate and thiosulfate in anaerobic culture conditions. Here we report in situ microscopic observations and measure the thermally activated (79 kJ mol^{-1}) precipitation kinetics of high yield (504 mg per liter of culture, 82% of theoretical maximum) extracellular As_2S_3 nanofibers produced by *Shewanella* sp. strain ANA-3, and demonstrate their potential in functional devices by constructing field effect transistors (FETs) based on individual nanofibers. The use of strain ANA-3, which possesses both respiratory and detoxification arsenic reductases, resulted in significantly faster nanofiber synthesis than other strains previously tested, mutants of ANA-3 deficient in arsenic reduction, and when compared to abiotic arsenic sulfide precipitation from As(III) and S^{2-}. Detailed characterization by electron microscopy, energy-dispersive X-ray spectroscopy, electron probe microanalysis and Tauc analysis of UV-vis spectrophotometry showed the biogenic precipitate to consist primarily of amorphous As_2S_3 nanofibers with an indirect optical band gap of 2.37 eV. X-ray diffraction also revealed the presence of crystalline As_8S_{9-x} minerals that, until recently, were thought to form only at higher temperatures and under hydrothermal conditions. The nanoscale FETs enabled a detailed characterization of the charge mobility ($\sim 10^{-5}$ cm^2 V^{-1} s^{-1}) and gating behavior of the heterogeneously doped nanofibers. These studies indicate that the biotransformation of metalloids and chalcogens by bacteria enables fast, efficient, sustainable synthesis of technologically relevant chalcogenides for potential electronic and optoelectronic applications.

1. Introduction

The synthesis of nanomaterials by biological or biomimetic means in physiological conditions offers multiple advantages over traditional physical and chemical strategies that typically require more extreme environments (temperature, pressure and pH). In addition to the promise of cheaper and greener synthesis processes, the resulting biogenic materials can exhibit unique morphologies and physical/chemical properties stemming from the tight control organisms exert over the composition, nucleation, crystallography and desired function of these materials [1]. While significant attention has been dedicated to understanding the synthesis and structure–function relations of the most abundant biominerals, especially carbonates and phosphates, the last decade has also witnessed additional interest in exploiting biological, especially microbial, strategies for producing a wider range of synthetic materials with technologically relevant mechanical, optical, electronic and magnetic functionalities [2–4]. Towards this goal, recent reports [5–7] demonstrated the synthesis of extracellular chalcogenide nanostructures with unique optoelectronic properties using a bacterial process relying on anaerobic respiration and detoxification activities to alter the oxidation states of the metal, metalloid and chalcogen precursors.

Chalcogenide compounds, resulting from the reaction of group VI elements (particularly S, Se and Te) with more electropositive elements (e.g. As, Sb, Si, Ge, Zn, Cd), represent an intriguing target for biogenic synthesis. Chalcogenides have been described as "chameleon" compounds because of their remarkable versatility: depending on composition and synthesis techniques they may be crystalline, glassy, metallic, semiconductive or ionic conductors

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[8]. This versatility leads to a wide range of tunable functionalities in various components including sensors, waveguides, photonic crystals [9] and photoactive devices [10–12]. Chalcogenide glasses are already commercially important in write-once and rewritable optical storage disks as well as phase-change memory relying on amorphous–crystalline transformations [8]. Some members of this family (e.g. As_2S_3) are infrared-transparent (700 nm–11.5 μm) and are therefore candidate materials for applications in infrared devices [9,13]. From an energy conversion standpoint, chalcogenides have been intensively investigated as photovoltaic materials for solar cells [12]. In addition, As_xS_y and As_xSe_y glasses have been reported to exhibit an optomechanical effect [10,11] for direct light-to-mechanical energy conversion when irradiated with polarized light matching the band gap energy. This phenomenon has been exploited to generate mechanical strain, resulting in all-optical (electricity-free) actuation of chalcogenide-coated cantilevers [10]. Further interest in unique and tunable size-dependent properties has motivated the development of quasi-one-dimensional (nanotube and nanowire) chalcogenides. The majority of these efforts, however, focus on physical and chemical synthesis techniques requiring templates, precursors, and hydro- or solvothermal methods, typically under relatively extreme conditions [14].

More recently, Hur et al. reported a microbiological route for synthesizing chalcogenide nanostructures by exploiting dissimilatory metal-reducing bacteria, specifically a number of *Shewanella* species, to produce an extracellular network of filamentous arsenic sulfide nanofibers/nanotubes in anaerobic culture conditions [5,6]. This process relies on the remarkable metabolic versatility of *Shewanella* [15,16] to concomitantly reduce $S_2O_3^{2-}$ to S^{2-} and As(V) to As(III). In this system, the thiosulfate $S_2O_3^{2-}$ serves as a terminal electron acceptor for respiration in lieu of O_2 under anaerobic conditions, resulting in S^{2-}, while arsenate reduction is thought to occur via As reductases tied to either the respiration or detoxification pathways of *Shewanella*. Rather surprisingly, it was reported that the resulting amorphous and polycrystalline nanostructures behaved as simultaneously metallic and semiconductive in terms of their electrical and photoconductive properties, respectively [5]. An additional report demonstrated the incorporation of more elements (Cd, Se) into As–S nanostructures through biogenic deposition and/or abiotic cation exchange to create ternary (As–S–Se and As–Cd–S) and quaternary (As–Cd–S–Se) composites [7]. Using X-ray absorption near-edge structure (XANES) and Fourier transformed extended X-ray absorption fine structure (EXAFS) analyses, the previous reports also confirmed the elemental oxidation states within the biogenic material to be consistent with As_2S_3 [5,7].

In this study, we present in situ microscopic observations to characterize the microbial synthesis of individual arsenic sulfide nanofibers, measure the synthesis kinetics, and detail the structural, crystallographic, electronic and band gap properties of the nanofibers resulting from the reduction activity of *Shewanella*. In contrast to previous detailed studies of chalcogenide synthesis by *Shewanella* sp. strain HN-41 [5,7], we focused our attention on *Shewanella oneidensis* MR-1 as well as *Shewanella* sp. strain ANA-3 and mutants of strain ANA-3 deficient in arsenic reduction. In addition to being genetically tractable, which will help shed light on the genetic and biomolecular mechanisms underlying nanomaterial synthesis, strain ANA-3 is widely regarded as the prototypical arsenic reducer, as a result of containing both the detoxification (encoded by *ars* genes) and respiratory (encoded by *arr* genes) As(V) reduction pathways [17–19]. The *ars* pathway is well characterized and known to be present in many bacteria [19,20]. Using this pathway, As(V) enters the cytosol by phosphate transporters and is reduced to As(III) by the arsenate reductase ArsC. As(III) is subsequently extruded from the cells by a cytoplasmic membrane efflux pump, ArsB, which may interact with an ATPase subunit, ArsA, to drive As(III) efflux using ATP hydrolysis. In contrast, the *arr* pathway has only been recently described [18,21]. The *arrAB* operon of strain ANA-3 encodes a large Mo-containing enzyme, ArrA, and an Fe–S protein, ArrB. Both ArrA and ArrB are required for respiratory reduction of As(V) [18,19]. The use of strain ANA-3 resulted in significantly more rapid precipitation of As–S nanofibers than previously reported under similar conditions. Furthermore, we demonstrate novel field-effect transistors (FETs) based on single biogenic nanofibers, and study their charge mobility and switching behavior as a function of backgating to identify the doping type and majority charge carriers in these semiconductors.

2. Materials and methods

2.1. Bacterial growth

A list of the bacterial strains and mutants used in this study is provided in Table 1. The inocula were grown aerobically in 20 ml of LB medium from a frozen (−80 °C) stock up to an optical density at 600 nm (OD_{600}) of 1.5 ± 0.15. These aerobic pre-cultures were inoculated at 0.1% (v/v) into anaerobic serum bottles each containing 80 mL HEPES-buffered (30 mM) medium consisting of: 20 mM sodium DL-lactate, as electron donor; 28 mM ammonium chloride; 1.34 mM potassium chloride; 4.35 mM sodium phosphate monobasic; 20 mM sodium hydroxide; 10 mM thiosulfate, as $Na_2S_2O_3{\cdot}5H_2O$; and 5 mM arsenate, as $Na_2HAsO_4{\cdot}7H_2O$. Vitamins, amino acids and trace mineral stock solutions were used to supplement the medium as described previously [22]. The medium was adjusted to an initial pH of 7.25, and anaerobic conditions were reached by purging with 100% N_2 for in excess of 45 min. The anaerobic serum bottles, sealed with butyl stoppers and aluminum seals, were sterilized by autoclaving at 120 °C for 15 min. Arsenate, thiosulfate and vitamins were added after autoclaving. All cultures were grown at 30 °C and agitated at a rate of 150 rpm.

2.2. Preparation of nanomaterials for EDS measurements, Tauc analysis and transistor microfabrication

For each preparation, 1 ml of the As–S precipitate was diluted in 14 ml of ultrapure water (Millipore Milli-Q Integral 5 purification system) and pelleted by centrifugation at 3000 RCF for 20 min. The samples were allowed to settle for a further 15 min before removing the supernatant. The samples were then washed eight times to remove salts, without further centrifugation, allowing 15 min between the addition and removal of ultrapure water for the material to settle at each step. For device fabrication, the resulting yellow precipitates were drop deposited on oxidized silicon chips for 5–15 min before removing the liquid by capillary action using a Kimwipe. The chips were then dried under nitrogen gas.

2.3. In situ microscopy of nanofiber synthesis

Microscopy observation chambers (500 μm height, 3 cm^2 surface area, 150 μl volume) were constructed by using double-sided tape (Scotch 3 M Permanent) to separate a coverslip (VWR No. 1) from the glass region of a glass-bottom Petri dish (WillCo Wells, GWSt-5030). A 1 mm diameter filling port was created by placing a 0.5 cm length of plastic microtubing in a drilled hole on the top of the Petri dish lid and fixing it in place with epoxy (Devon 5 Minute Gel). All components were sterilized in ethanol and allowed to dry before cell injection. An overnight culture of strain ANA-3 was grown in LB medium to OD_{600} 2.0 and inoculated into the anaerobic defined medium described above at 1% (v/v). Subsequent chamber filling and assembly was performed in a nitrogen bag,