

Size-Selective Electrochemical/Chemical Synthesis and Optical Characterization of MoS₂ Nanoribbons

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- This project aims to develop a synthesis of ultra-long molybdenum disulfide nanowires for use in optical devices and chemical sensors. We also seek to elucidate the fundamental electronic and optical properties of these nanoribbons that might be exploited in practical applications.

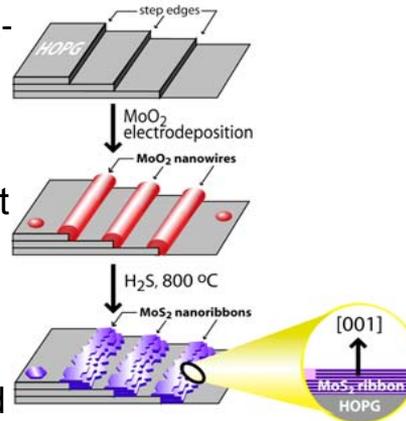


Figure 1. Schematic of the E/C synthesis of MoS₂ nanoribbons

Figure 2. SEMs of MoO₂ nanowires and the MoS₂ nanoribbons derived from them.

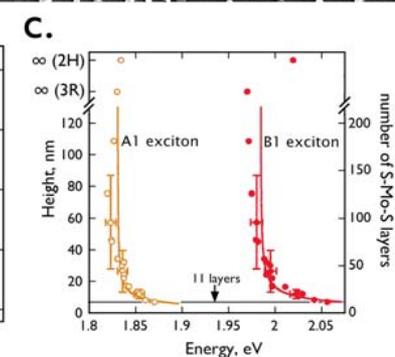
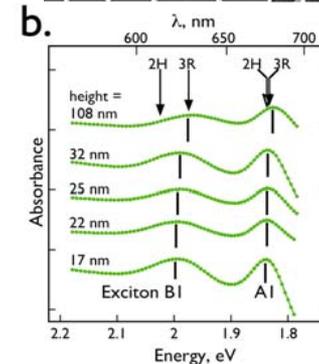
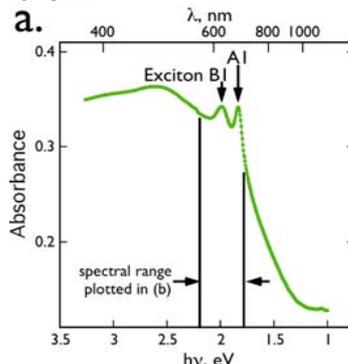
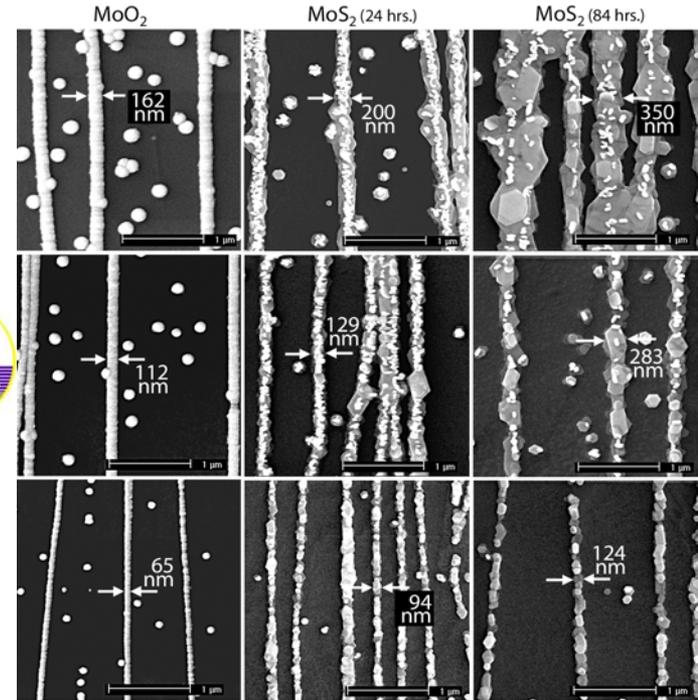


Figure 3. Absorbance spectra (a & b) of MoS₂ nanoribbons and plot of exciton energies as a function of the ribbon thickness (c).

- Molybdenum disulfide nanowires and nanoribbons have been synthesized by the two-step, Electrochemical/Chemical synthetic method shown in Figure 1. In the first step, MoO₂ wires were electrodeposited size-selectively by electrochemical step edge decoration on a highly oriented pyrolytic graphite (HOPG) surface. Then MoO₂ precursor wires were converted to MoS₂ by exposure to H₂S above 800°C producing MoS₂ nanoribbons (as shown in Fig. 2). These MoS₂ nanoribbons were more than 50 μm in length and were organized into parallel arrays containing hundreds of wires or ribbons. Optical absorption measurements of MoS₂ nanoribbons (Fig. 3) reveal a direct gap near 1.95 eV and two exciton peaks, A1 and B1, characteristic of 3R-MoS₂. These exciton peaks shifted to higher energy by up to 80 meV as the wire thickness was decreased to 7 nm (eleven MoS₂ layers).

Aim of the project:

MoS₂ has tremendous potential for a variety of applications in nanoscience because of its incredible environmental stability. While MoS₂ is similar in its electronic properties to silicon (an indirect bandgap of 1.2 eV versus 1.12 eV for silicon), it is composed of S-Mo-S layers, disposed in van der Waals contact, with coordinately saturated surfaces that resist oxidation even at temperatures up to 85°C and under illumination in water.

While MoS₂ nanowires have been synthesized previously by Tenne and coworkers, in all cases fullerene tubes have been obtained. We have developed the first synthesis of ribbons of MoS₂ that have the same crystal structures (3R) as bulk MoS₂. Our objective now is to characterize the optical and electrical properties of these nanostructures that are relevant to their performance in devices such as chemical sensors and photodetectors.

Research results:

Nanoribbons of MoS₂ were obtained by electrodepositing hemicylindrical MoO₂ nanowires using our *Electrochemical Step Edge Decoration (ESED)* method. Then we converted these precursor nanostructures into MoS₂ nanoribbons by exposure to H₂S at 800-900 °C. The resulting nanoribbons have one of the crystal structures (namely 3R) seen for bulk, naturally occurring MoS₂. These ribbons are long (many more than 500 μm), are organized into parallel arrays, and are obtained with size selectivity. Other conclusions of our work so far include the following:

MoS₂ nanoribbons were obtained with size-selectivity since the final dimensions of the nanowire depend on the dimensions of the MoO₂ nanowire from which it was synthesized, and the diameter of the MoO₂ nanowires is proportional to the square root of the electrodeposition duration. "Populations" of MoS₂ nanowires were narrowly dispersed in terms of their lateral dimensions. RSD values for the ribbon height, for example, were <20%.

Each synthesis of MoS₂ nanoribbons produces hundreds of ribbons that are approximately straight and organized into parallel arrays on the graphite surface. These nanowires adhere weakly to the graphite, and may be transferred without loss of registry to cyanoacrylate-coated glass surfaces for electrical or optical characterization.

MoS₂ nanoribbons show optical absorption spectra in which the A1 and B1 exciton transitions characteristic of bulk MoS₂ are clearly observed. This is true even for nanoribbons consisting of just eleven layers. The energies of these exciton peaks increase from the value characteristic of bulk 3R-MoS₂ and in direct proportion to 1/L_{||}². Our measurements yield effective mass values of μ_{||}^{A1} = 0.198 m_o and μ_{||}^{B1} = 0.105 m_o, corresponding to exciton Bohr radii of 1.3 nm (A1) and 2.5 nm (B1).

Electrical contact has been made to these nanowires to enable electrical measurement. The temperature dependant I-V data shows thermally activated conduction with activation energies that were dependant on the morphology of the nanowires and varied from 126 meV for incompletely converted nanowires to 26 meV for annealed and highly crystalline nanoribbons.

Significance of this work:

We have developed a new and potentially type of semiconducting nanowire that mimics the electronic properties of silicon, while possess vastly superior properties with respect to its environmental stability.

Electrodeposition of Bi_2Te_3 Nanowires

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• The objective of this work is to synthesize ultra-long Bi_2Te_3 nanowires. Such wires should exhibit unusually efficient thermoelectric behavior, but wires of millimeter length are required to test this prediction.

• We have developed a method for preparing arrays of hundreds of Bi_2Te_3 nanowires that are 100 - 300 nm in diameter and up to 1 mm in length. This method involves the electrodeposition of Bi_2Te_3 selectively at the step edges present on a graphite surface, as shown schematically in Figure 1. Stoichiometric Bi_2Te_3 is obtained using a two-step procedure in which Bi_2Te_3 and excess bismuth are both deposited in step 1, and then just the excess bismuth is stripped from this deposit in step two. Typical nanowires are shown in Figure 2. The diameter of these nanowires can be controlled over the range from 100 nm to 300 nm by adjusting the number of deposition/stripping cycles as shown in Figure 3. We have used electron diffraction coupled with EDX to confirm the structure and composition of these nanowires.

(Menke et al. *Nanoletters* 4 (2004) ASAP)

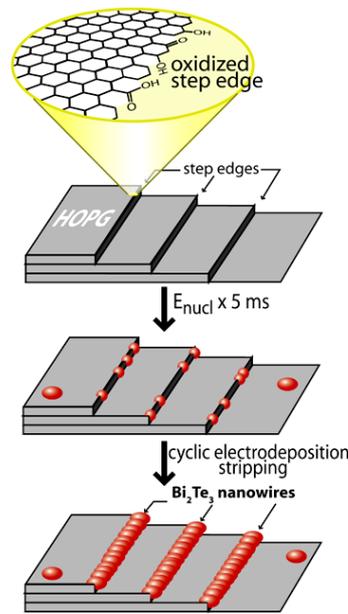


Figure 1.

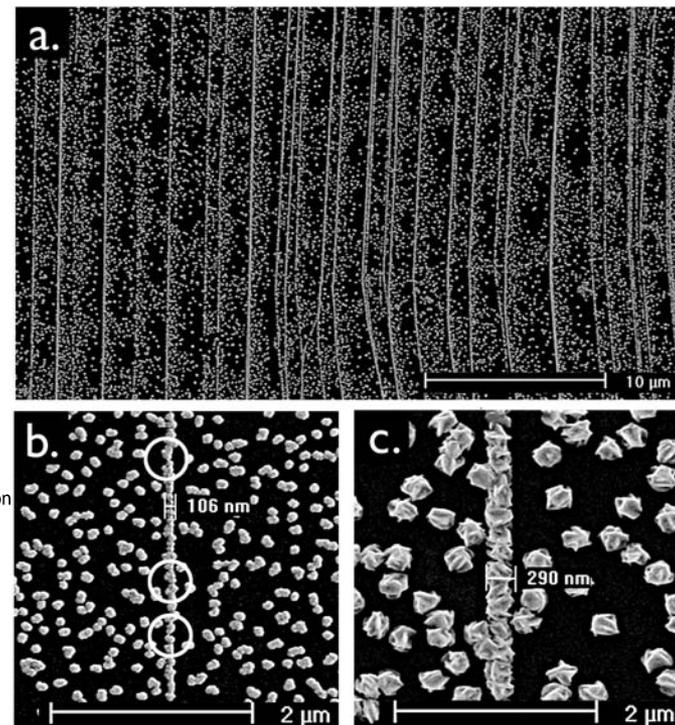
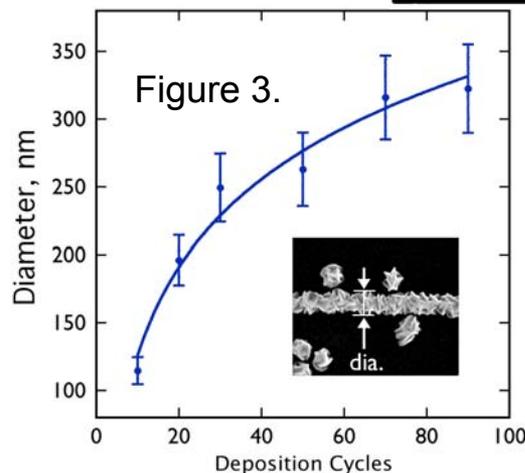


Figure 2.

Figure 1. Schematic diagram of the *Electrochemical Step edge Decoration (ESED)* Method used for preparing Bi_2Te_3 nanowires.

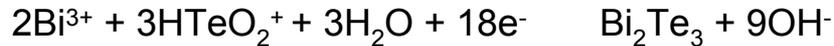
Figure 2. SEM images of Bi_2Te_3 nanowires. b) 10 cycles, c) 90 cycles.

Figure 3. Plot of diameter vs. number of electrodeposition-/stripping cycles.



Aim of the project:

Theory predicts that Bi₂Te₃ nanowires will exhibit a higher thermoelectric figure of merit (called “ZT”) than bulk films of this material. These predictions - which have remained untested - have stimulated interest in the synthesis of Bi₂Te₃ nanowires. Up until now, template synthesis has been exclusively used to obtain Bi₂Te₃ nanowires by both Martin and Stacy who electrodeposited Bi₂Te₃ into the pores of a porous alumina membranes. Both research groups employed an electrodeposition recipe similar to that originally described by Magri et. al.:



Nanowires with minimum diameters of 280 nm and 40 nm, respectively, were obtained by these two research groups whereas the lengths of the nanowires prepared by template synthesis range from 10 to 50 μm. However, calculations by Rowe et al. demonstrate that efficient thermoelectric devices are likely to require nanowires that are not only extremely narrow, but also extremely long - up to 1 millimeter in length - and such long Bi₂Te₃ nanowires have never before been prepared. Our objective is to prepare such ultra-long Bi₂Te₃ nanowires and to measure ZT for them as a function of the critical geometrical parameters such as length, diameter, and morphology.

Research results:

We have described a method for preparing arrays of hundreds of Bi₂Te₃ nanowires that are 100 - 300 nm in diameter and up to 1 mm in length. This method, a variant of the electrochemical step edge decoration (ESED) developed with DMR-9876479 in our lab, involves the electrodeposition of Bi₂Te₃ selectively at the step edges present on a graphite surface. The potential program for our method consists of three steps: 1) Mild oxidation of the basal plane step edges on a piece of highly oriented pyrolytic graphite (HOPG) at +0.80V for 5 s (this increases the nucleation density along steps); 2) Nucleation of nanoscopic Bi₂Te₃ particles along the oxidized step edges at -0.60 V for 5 ms (these nuclei are the seeds from which nanowires will emerge); 3) Codeposition of Bi₂Te₃ and excess bismuth on these seeds during a negative-going potential scan from +0.3 to -0.05 V and subsequent anodic stripping of excess bismuth – producing a stoichiometric Bi₂Te₃ deposit - during a positive-going potential scan from -0.05 V to 0.30 V. Step 3 is then repeated for 10-100 cycles depending on the diameter of the Bi₂Te₃ that are targeted. This cyclic electrodeposition/stripping strategy is identical in concept to the method described by Mike Sailor for the electrodeposition of stoichiometric thin films of CdSe in 1991.

Significance of this work:

The Bi₂Te₃ we have synthesized will permit the first quantitative evaluation of nanowires for thermoelectric applications. We are ready now to begin this evaluation of the thermoelectric properties as a function of their diameter, their length, the presence of dopant species (e.g., Se and Sb), and finally the morphology of these nanowires (e.g., their roughness).