

# TOWARDS BULK SYNTHESSES OF NANOMATERIALS: AN HOMEOSTATICALLY SUPERSATURATED SYNTHESIS OF POLYMER-LIKE $\text{Bi}_2\text{S}_3$ NANOWIRES WITH 100% YIELD AND NO INJECTION.

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## SUPPORTING INFORMATION

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### *MATERIALS AND METHODS*

#### **SYNTHESES:**

For all the syntheses (hot-injection route and one-pot route) carried out in this study, the reaction temperature used was 90°C and the reactions were performed in a 3-necked round-bottom flask with two of the side necks capped with septa and the central neck connected to a condenser.

(1) Hot-injection route: The hot-injection route for the synthesis of  $\text{Bi}_2\text{S}_3$  nanowires was previously reported<sup>1</sup>. All chemicals used for the hot-injection route were from Sigma-Aldrich.

Briefly, 21.608 g of bismuth (III) citrate (99.99%) was added to 71.92 mL of OLA (technical grade-70%) under stirring. After air was purged, the system was put under vacuum and heated up to 100 °C. The system was then left under vacuum at 100 °C for 30 min followed by being kept at 160 °C for 30 min under nitrogen atmosphere. Then the obtained mixture was cooled down to 130 °C under nitrogen atmosphere, and a sulfur solution made of 8.538 g sulfur (99.98%) and 178.08 g OLA (technical grade, 70%) was quickly injected into the flask. After the injection, the flask was put in a 90 °C oil bath. The reaction was quenched after 14 hr of reaction by pouring out the reaction product into ~500 mL cold toluene.

(2) One-pot route: In order to test the robustness of the one-pot route, three reactions using chemicals with different purity levels (from different suppliers) were carried out. The combinations of chemicals used for each reaction are as follows. #1 reaction: OLA from Sigma-Aldrich (technical grade, 70%), bismuth (III) citrate from Sigma-Aldrich (99.99%), sulfur from Sigma-Aldrich (99.98%). #2 reaction: OLA from Acros (C18-content 80-90%), bismuth (III) citrate from Sigma-Aldrich (99.99%), sulfur from Sigma-Aldrich (99.98%). #3 reaction: OLA from ChemCruz ( $\geq 68\%$ ), bismuth (III) citrate from Amresco (high purity grade), sulfur from Acros (99.5+%).

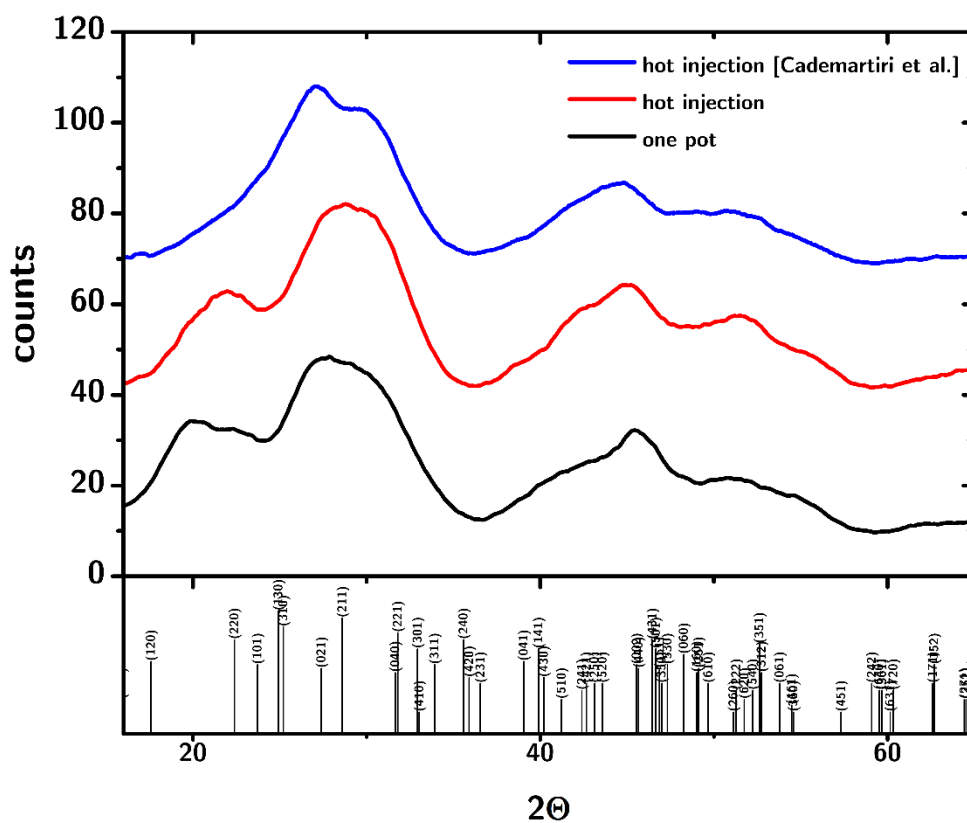
Typically, 250 mL of OLA, 10.109 g of bismuth (III) citrate, and 48.759 g of sulfur were subsequently added into the reaction flask under stirring. Then the flask was put in a 90 °C oil bath. The stirring was allowed to stop naturally with the increase in viscosity during the reaction. After 14 hr, the reaction was quenched by pouring out the reaction product into ~500 mL cold toluene. A spatula was needed in the process as the reaction product was highly viscous.

## CHARACTERIZATION

Uv-Vis absorption spectra of the samples were determined using an Agilent 8453 UV-Vis Spectrophotometer at Chemical Instrumentation Facility at Iowa State University. All samples were purified according to a previously reported procedure<sup>1</sup> before measuring the Uv-

Vis absorption spectra in order to remove the influence of excess sulfur. As the one-pot route used significantly more sulfur compared with the hot-injection route, samples collected at later stages (after 2 hr of reaction) from the one-pot reactions were purified more than once. Toluene with ~6% (v/v) OLA was used to facilitate the redispersion of the precipitated Bi<sub>2</sub>S<sub>3</sub> NWs during purification. Absorbance at 533 nm in the Uv-Vis spectra was used to determine the yield by using the previously reported extinction coefficient<sup>2</sup>. Transmission electron microscopy (TEM) images were obtained using a 2007 JEOL 2100 200 kV STEM in TEM mode at 200 kV at the Microscopy and NanoImaging Facility at Iowa State University. X-ray diffraction (XRD) was performed at the CIF at ISU using Rigaku Ultima IV X-Ray Diffractometer with 2 $\theta$  in the range of 15-65°, a scan speed of 0.5°/min, and a sampling width of 0.0200°.

SUPPORTING FIGURES



**Figure S1. XRD characterization of the product.** The plot compares the XRD diffraction from the  $\text{Bi}_2\text{S}_3$  nanowires obtained from the one-pot strategy (black line) and the hot injection approach (red line). In blue are shown the original XRD spectrum reported in the original report of the synthesis of  $\text{Bi}_2\text{S}_3$  nanowires<sup>2</sup>. The additional feature at  $20^\circ$  is attributable to an amorphous phase.

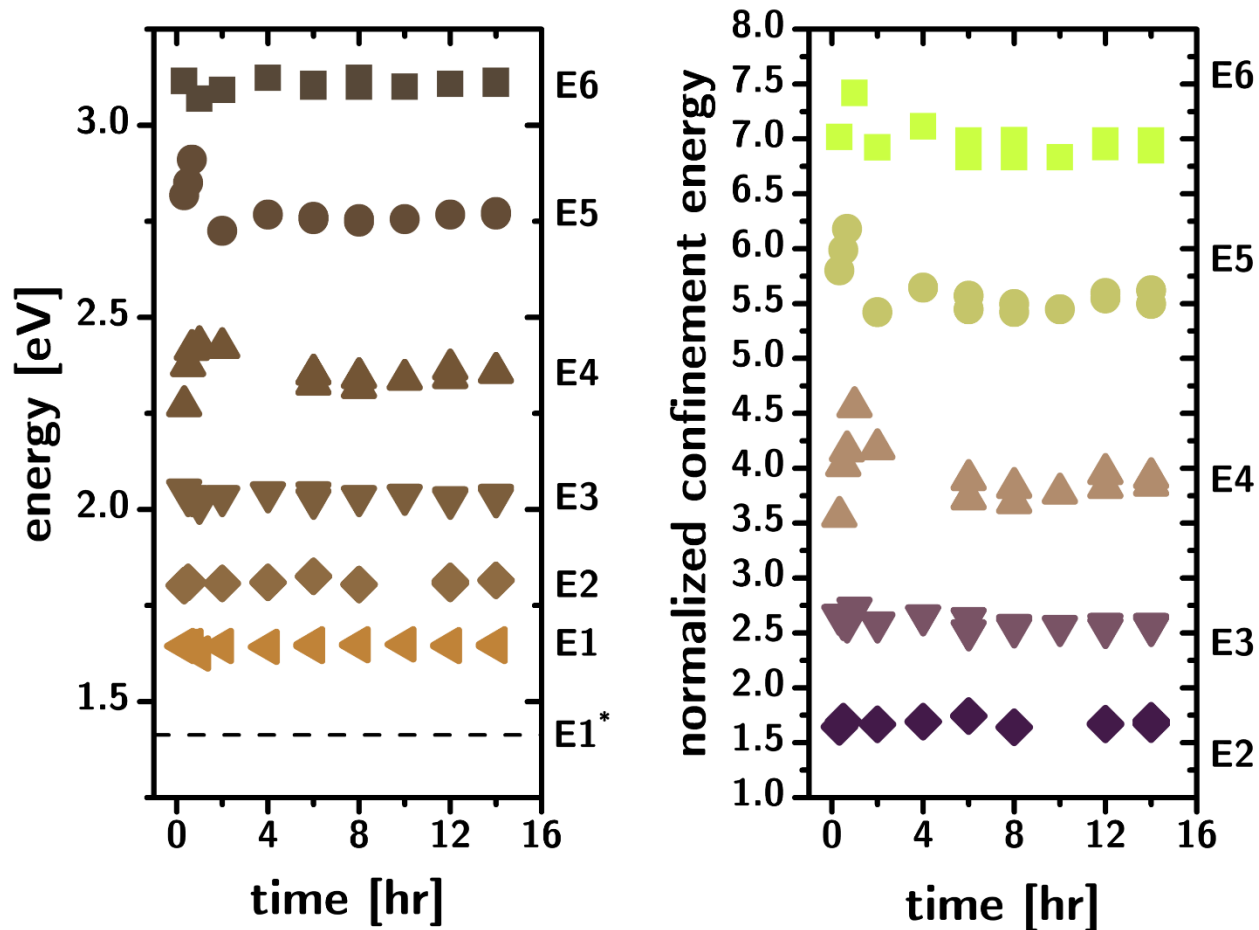


Figure S2. Optical properties of  $\text{Bi}_2\text{S}_3$  nanowires. (left) Energy of the six excitonic transitions as a function of the time of growth of the nanowires (one pot strategy).  $E1^*$  identifies the exciton energy of bulk  $\text{Bi}_2\text{S}_3$ . (right) Normalized confinement energy of the five highest energy levels.

## REFERENCES

1. Cademartiri, L.; Guerin, G.; Bishop, K. J. M.; Winnik, M. A.; Ozin, G. A., Polymer-like conformation and growth kinetics of  $\text{Bi}_2\text{S}_3$  nanowires. *J. Am. Chem. Soc.* **2012**, 134, (22), 9327-9334.
2. Cademartiri, L.; Malakooti, R.; O'Brien, P. G.; Migliori, A.; Petrov, S.; Kherani, N. P.; Ozin, G. A., Large-scale synthesis of ultrathin  $\text{Bi}_2\text{S}_3$  necklace nanowires. *Angew. Chem. Int. Edit.* **2008**, 47, (20), 3814-3817.