

Antimony Selenide Nanostructures: morphology control through modulation of ligand chemistry and variation of precursor ratio

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Supporting Information

EXPERIMENTAL SECTION

General: all chemical manipulations were carried out under dry nitrogen using conventional Schlenk-line and glove box techniques. The following chemicals: selenourea (98%), antimony (III) chloride (99.95%), oleic acid (90%), oleylamine (70%), 1-octadecene (90%), and tri-*n*-octylphosphine oxide (99%) were purchased from Aldrich Chemicals and used without further purification. Manipulations of antimony-based nanomaterials were carried out using extra-dry solvents (ethyl alcohol, toluene and hexanes), which were purchased from Acros Organics and used without additional purification. TEM imaging was performed using a FEI Tecnai F-20 TEM. Absorbance spectra were recorded using a Perkin Elmer Lambda 950 spectrophotometer. XRD characterization was performed using a Panalytical X'Pert X-Ray Diffractometer.

Preparation of nanorods: This reaction was carried out entirely in a nitrogen filled glovebox. 0.87 mmol (200 mg) of antimony (III) chloride was dissolved in 3 mL of oleic acid at 150 °C. In a separate flask, 0.81 mmol (100 mg) of selenourea was dissolved in 1 mL of oleylamine at 200

°C. After formation of a dark red solution, this mixture was cooled to 100 °C. Next, the antimony precursor was heated to 180 °C after which the selenium precursor was rapidly injected to initiate the reaction. After 10 sec the reaction was quenched by rapid addition of toluene (4 mL). Further extension of growth periods afforded both larger particles and insoluble products. The purification of the nanorods and other nanoparticles of antimony selenide was carried out in a nitrogen filled glovebox using a standard technique including addition of ethanol, centrifugation and redispersion in toluene or hexane. Within the presented reaction procedure, it was established that the window for the reaction conditions (temperature) is very narrow such that small variations may lead to aggregation products.

Preparation of nanocrystals: 0.58 mmol (0.13 g) of antimony(III) chloride, 0.75 mL of oleylamine, 0.55 mL of oleic acid, and 6.3 mL of 1-octadecene were placed in a 25 mL 3-neck round bottom flask equipped with a stirring bar, rubber septum and thermocouple in the glovebox. The flask was sealed, removed from the glovebox and heated under vacuum at 130 °C for 30 min using a heating mantle. Next, the reaction was pump/purged three times with N₂ and the temperature was slowly increased to 150 °C under vacuum, then switched to N₂ and heated to 180 °C. At this point the reaction solution appeared clear. Separately, a solution containing 1.62 mmol (0.20 g) of selenourea in 1.25 mL of oleylamine was prepared in the glovebox at 150 °C. The Se-containing precursor solution was quickly removed from the glovebox and rapidly injected into the reaction flask at 180 °C and the reaction was immediately quenched by injection of hexane (3 mL). The reaction period could be extended to several seconds to yield larger nanoparticles. The elimination of oleylamine from the reaction mixture leads to the formation of smaller nanorods (see Figure 2 of Supporting Information).

Preparation of nanospheres: 0.58 mmol (0.13) g of antimony(III) chloride, 0.75 mL of oleylamine, 0.55 mL of oleic acid, and 6.3 mL of 1-octadecene (ODE) were placed in a 3-neck round bottom flask equipped with a stirring bar and thermocouple in the glovebox. The flask was sealed, removed from the glovebox and heated under vacuum at 130 °C for 30 min using a heating mantle. Next, the reaction was pump/purged three times with N₂ and the temperature was slowly raised to 150 °C under vacuum, then switched to N₂ and heated to 180 °C. At this time the solution appeared clear. Separately, a solution containing 1.22 mmol (0.15 g) of selenourea in 1.25 mL of oleylamine was prepared in the glovebox at 150 °C. The Se-containing precursor solution was rapidly injected into the reaction flask at 170 °C. After 10 seconds the reaction was quenched by the injection of hexane (3 mL).

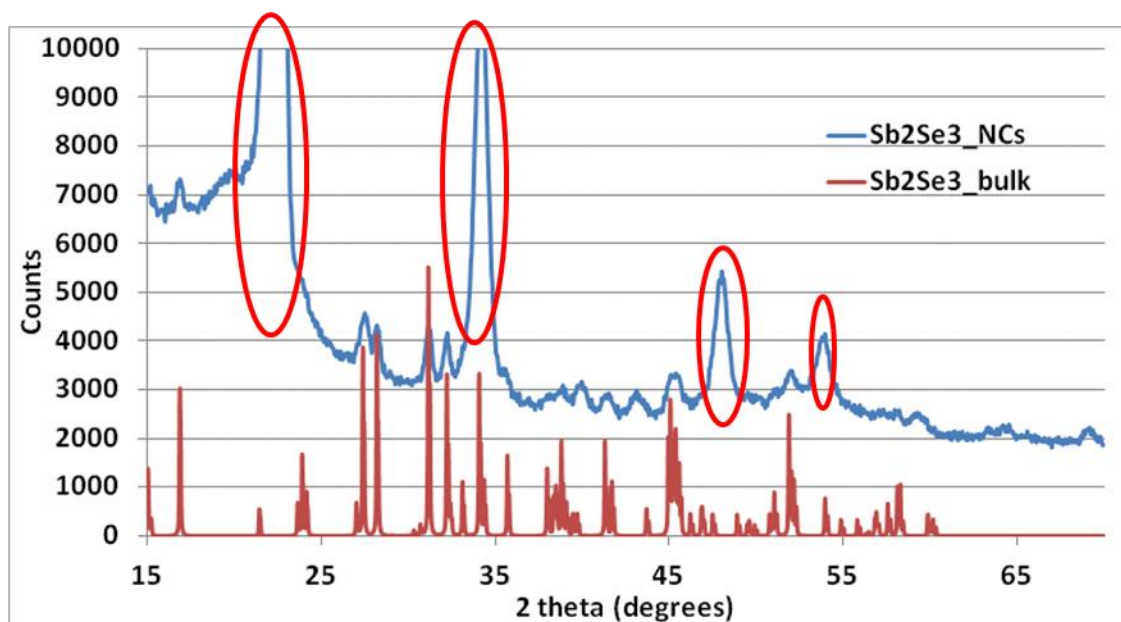


Figure 1. XRD characterization of nanocrystalline antimony selenide (nanorods) deposited on a Si substrate in comparison with bulk material where the circled peaks correspond to the substrate.

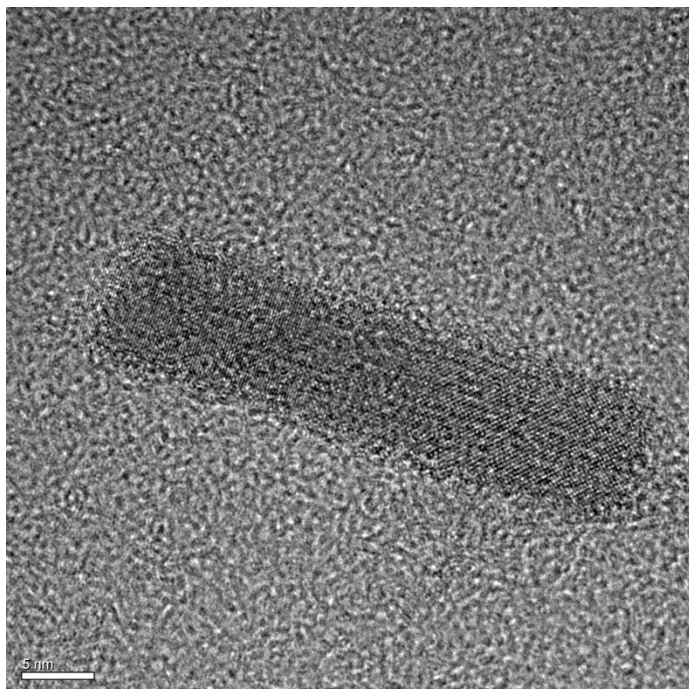


Figure 2. TEM image of an antimony-selenide nanorod obtained through adjustment of the synthesis procedure.

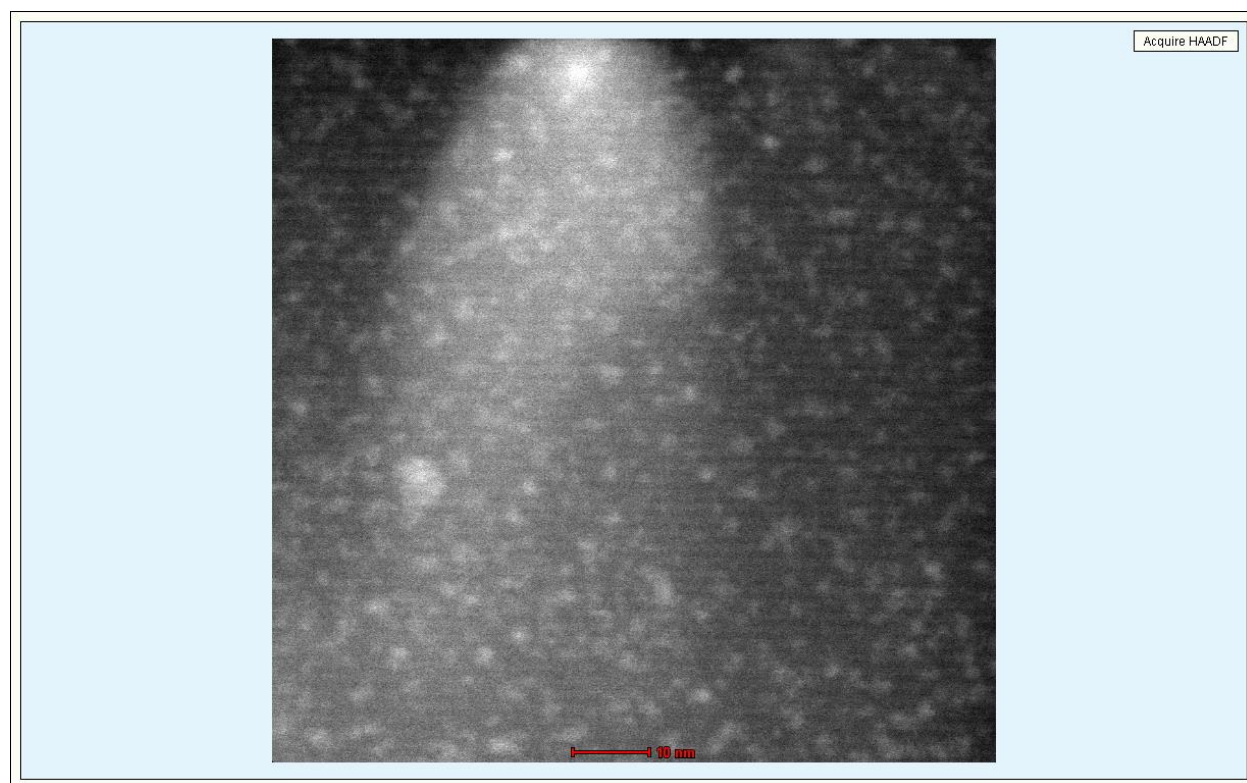


Figure 3. STEM image of ultra-small (“magic-sized”) antimony-selenide nanoparticles.

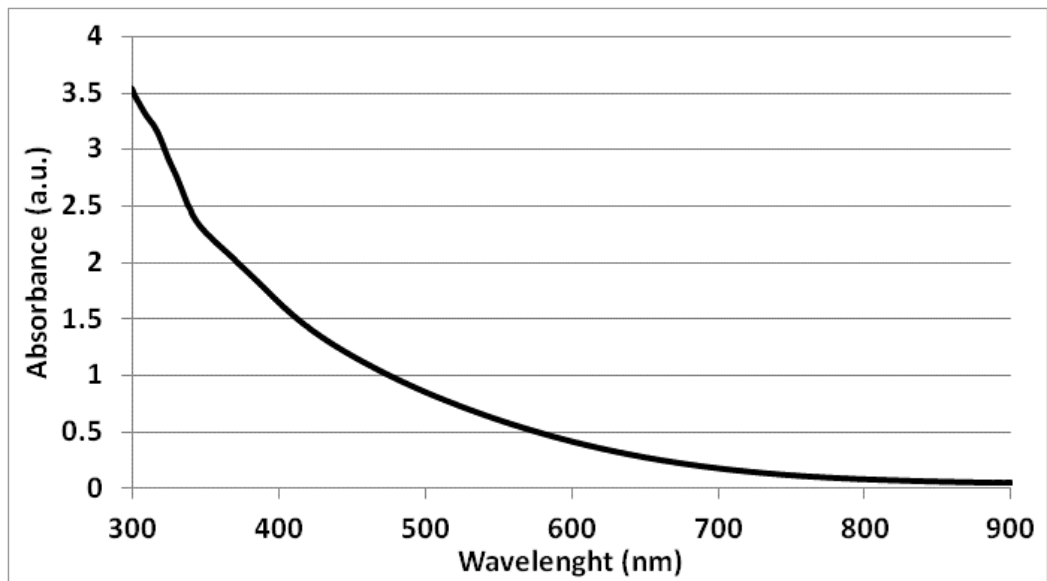


Figure 4. Absorbance spectra of antimony selenide nanoparticles.

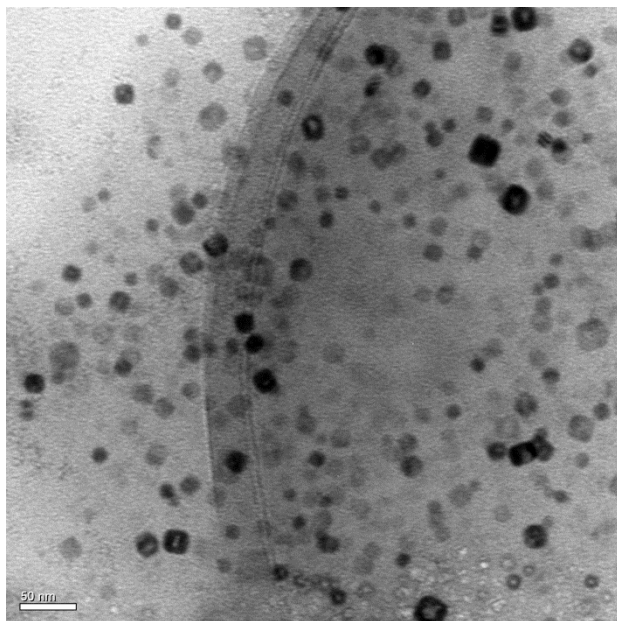


Figure 5. Low magnification TEM image showing a plurality of antimony selenide nanospheres.