Supporting Information for

Synthesis of Monodisperse SnTe nanocrystals: A New Example of Narrow Gap Semiconductor Quantum Dots

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Experimental details:

Chemicals and materials. Bis[bis(trimethylsilyl)amino]tin(II), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OLA, 70%), Tellurium (granular, 99.999%), tetrachloroethylene (TCE, spectrophotometric grade, $\geq 99\%$), tetrachloromethane ($\geq 99.5\%$) and unhydrous acetonitrile were purchased from Aldrich. Trioctylphosphine (TOP, 97%) was obtained from Strem. Methanol, acetone, hexane, chloroform, and ethanol were of analytical grade and obtained from various sources. All chemicals were used as received without any further purification. Octadecene was vacuum dried at 140°C for 2 hours and stored in a nitrogen glovebox.

Synthesis of SnTe nanocrystals. All experiments were carried out using standard airless techniques: a vacuum/dry nitrogen gas Schlenk line was used for the synthesis and a nitrogen glove-box for storing and handling air- and moisture-sensitive chemicals. The TOPTe solution (10% of Te in TOP) was prepared in a glove-box by dissolving elemental tellurium in TOP at 200°C for 2 hours. A tin(II) injection solution was prepared by dissolving 0.16 mL (0.4 mmol) of bis[bis(trimethylsilyl)amino]tin(II) in 6 mL of dry ODE. This solution was loaded into a syringe and injected into the hot reaction mixture.

In a typical synthesis of SnTe NCs, 14 mL of oleylamine (or oleylamine/octadecene mixture) were placed into a 100 mL three-neck flask, degassed and dried under vacuum for 1 hour at 100°C . 1 mL of a TOPTe solution (0.73 mmol referring to Te) was added with a syringe. The temperature was raised to $150\text{--}180^{\circ}\text{C}$ and the Tin(II) injection solution was swiftly injected under vigorous stirring. After injection the temperature dropped to $120\text{--}150^{\circ}\text{C}$ and the reaction was terminated typically after 1.5 min. 3 mL of OA were added to the cold solution. A chloroform/acetone mixture (1:1) was added to the crude solution and the NCs were isolated by centrifuging. The NCs were additionally purified twice by redispersing them in chloroform and precipitating with acetone. Finally, the particles were dissolved in nonpolar solvents forming stable concentrated colloidal solutions.

Preparation of SnTe NC superlattices. A substrate (e.g. carbon coated TEM grid) was placed in a glass vial containing colloidal solution of SnTe NCs. The vial was tilted by 60-70 degrees in a low-pressure chamber. Ordered superlattices formed upon evaporation of the solvent. Toluene and mixtures of toluene with tetrachloroethylene or chloroform were used as solvents ($\sim 1:1$ by volume). The superlattices were obtained by evaporating relatively concentrated colloidal solutions at $\sim 50^{\circ}\text{C}$ under reduced pressure (~ 3.2 kPa).

Structural, optical and electronic characterization of SnTe nanocrystals. Samples for TEM characterization were prepared by placing 1-2 μL of a diluted (0.1 mg/mL) NC solution in toluene or TCE onto a carbon-coated copper grid (Ted-Pella). The excess of solvent was removed after 10 s by a filter paper. TEM and HRTEM pictures were obtained using a JEOL 2011 TEM microscope operating at an acceleration voltage of 200 kV. EDX elemental analysis was performed on a JEOL JSM-6400 SEM microscope. For optical absorption measurements, intensively washed NCs were redispersed in tetrachloromethane or TCE. Linear optical absorption spectra were taken using a BOMEM DA8 Fourier transform infrared spectrometer operating from 10000 to 400 cm^{-1} . Wide-angle powder XRD patterns are

collected using a Bruker D8 diffractometer with a GADDS area detector. Samples for electrical measurements were prepared by depositing a ~100 nm thick film of close-packed SnTe NCs by drop casting a NC solution in a hexane/octane (~9:1 vol.) mixture on highly doped Si wafers with a 110 nm thick SiO₂ thermal gate oxide. Source and drain Ti/Au (70/450Å) electrodes were lithographically patterned on the SiO₂ surface prior to the NC deposition. Close-packed SnTe NC films were treated with hydrazine by dipping the wafers into 0.5M solution of hydrazine in acetonitrile. The duration of the treatment varied from 12 to 72 hours, followed by rinsing the device with anhydrous acetonitrile. The hydrazine-treated NC film is insoluble in common solvents such as hexane and chloroform. Due to reduction in interparticle spacing, treated nanocrystal film exhibited some cracks (Figure S4). The freshly hydrazine-treated NC films were dried under nitrogen at 80°C for 1 hour. To further improve the electrical conductivity these cracks could be filled by depositing more SnTe NCs. Then, additional SnTe NC solution was cast on top of the hydrazine treated NC film. After depositing the second layer and drying, the hydrazine treatment was repeated. Imaging of the NC film in high-resolution SEM shows that the cracks are filled with SnTe nanocrystals. Field-effect devices were tested using an Agilent 4156B semiconductor parameter analyzer. The source electrode was grounded. All room temperature electrical measurements were performed under dry nitrogen atmosphere.

Figure S1. Representative low-resolution TEM images of (a) 4.7 nm, (b) 7.2 (c) 10.4 and (d) 14.1 nm large monodisperse SnTe NCs.

Figure S2. EDX analysis of SnTe nanocrystals confirms their nearly stoichiometric composition. Fitting the measured spectrum yields a composition of $\text{Sn}_{0.54}\text{Te}_{0.46}$ with a 5% standard error.

Figure S3. An experimental summary of the effect of the reaction temperature and the stabilizer (oleylamine) concentration on the size of the SnTe NCs.

As-deposited

After the hydrazine treatment

Figure S4. High-resolution SEM images of a SnTe NC film (a) before and (b) after treatment with a 0.5M solution of hydrazine in anhydrous acetonitrile. Such a treatment enhanced the conductance of the SnTe NC film by 6 orders of magnitude.

Figure S5. Plot of drain current I_D vs. drain-source voltage V_{DS} , as a function of gate voltage V_G for a SnTe NC field-effect transistor whose channel is comprised of 12 nm SnTe nanocrystals treated with a 0.5M hydrazine solution for 72 hours (channel length $L=2.5\ \mu\text{m}$, width $W=20000\ \mu\text{m}$, 110nm thick SiO_2 gate dielectric).

Figure S6. (a) TEM image, (b) Powder XRD and (c) optical absorption spectra of SnSe NCs synthesized by a reaction of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and trioctylphosphine selenide in oleylamine.