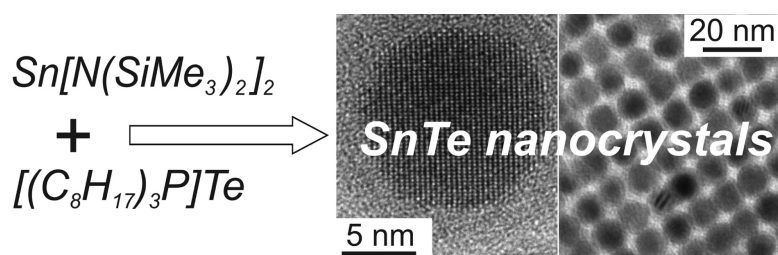## Communication

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SnTe Nanocrystals: A New Example of Narrow-Gap Semiconductor Quantum Dots

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Over the past decade a significant progress in the synthesis of narrow gap IV−VI (PbS, PbSe, PbTe),[1] II−VI (HgTe, Cd$_x$Hg$_{1-x}$Te),[2] and III−V (InAs)[3] nanocrystals (NCs) triggered a recognition of their high potential for various optical,[4] electronic,[5] and optoelectronic[6] applications. Typically, the band gaps of these NCs can be tuned between 0.5 and 1.5 eV, covering the entire near-infrared (near-IR) spectral region.[7] The synthesis of colloidal NCs with band gap energy below 0.5 eV is still a challenge, with only limited information available.[8,9] At the same time, narrow-gap semiconductor NCs are highly desirable for photovoltaic, thermovoltaic, and thermoelectric[10] devices as well as numerous optical applications. The recent discovery of efficient carrier multiplication in semiconductor quantum dots placed narrow-gap NCs among the most promising materials for thin-film photovoltaics.[11]

Bulk SnTe is a IV−VI semiconductor with a direct band gap of 0.18 eV at 300 K[12]. It is used in mid-IR photodetectors[13] and thermoelectric heat converters.[14] The previous attempts to synthesize SnTe NCs did not yield uniform particles of controllable size.[15] Here we report a solution-phase synthesis of high-quality colloidal SnTe NCs with mean diameters tunable in the range of ca. 4.5−15 nm and corresponding band gaps of 0.8−0.38 eV.

As a tin(II) source, we used commercially available Sn-[N(SiMe$_3$)$_2$]$_2$, bis[bis(trimethylsilyl)amino]tin(II), also known as Lappert's stannylene.[16] Our initial attempts to synthesize tin chalcogenides by using less reactive precursors like tin oleate, acetate, or chloride failed because of an improper balance between nucleation and growth rates of the NCs. The synthesis of SnTe NCs is based on the reaction of Sn[N(SiMe$_3$)$_2$]$_2$ and trioctylphosphine telluride (TOPTe) in oleylamine (OLA). In a typical synthesis,[17] 0.4 mmol of Sn[N(SiMe$_3$)$_2$]$_2$ dissolved in 6 mL of octadecene (ODE) were injected into a three-neck flask containing a solution of 0.7 mmol of TOPTe in 14 mL of OLA, kept at 150 °C. The almost instantaneous nucleation was followed by a temperature drop to about 120 °C. The reaction was kept at this temperature for 1−2 min and rapidly cooled to room-temperature. A 3 mL aliquot of dried oleic acid (OA) was added to efficiently passivate the NC surface. The SnTe NCs were isolated and purified using the standard solvent/nonsolvent procedure.[17]

The as-synthesized SnTe NCs have uniform, nearly spherical shapes (Figure 1a,b). The NCs size distribution was typically below 10% without any size-selection steps (Figure S1, Supporting Information). An analysis of the powder X-ray diffraction (XRD) patterns (Figure 1c) and high-resolution TEM images (Figure 1d,e) revealed the cubic rock-salt crystal structure, identical to that of bulk SnTe (space group *Fm3m*, *a* = 6.235 Å).[12] The NC sizes estimated from the broadening of the XRD reflections were consistent with those deduced from TEM images, indicating a high
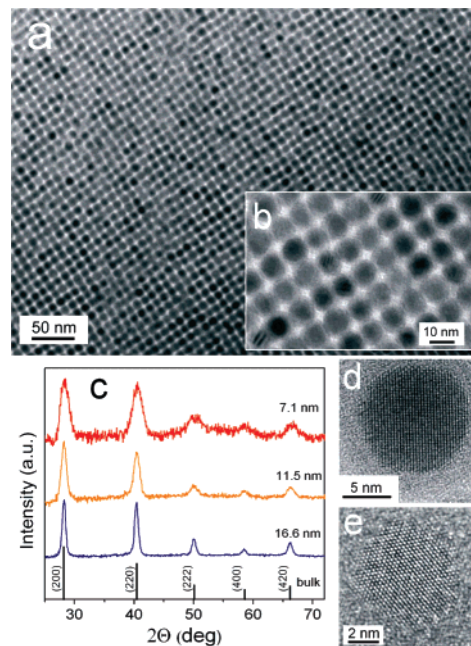
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Figure 1. (a,b) TEM images of a superlattice of 10.2 nm SnTe NCs capped with oleic acid. (c) Powder XRD patterns of SnTe NCs with various sizes. The sizes indicated above each curve are estimated by the Scherrer equation, applied to the width of the [100] peaks. The vertical lines indicate the corresponding reflection positions and intensities for bulk SnTe. (d,e) Representative high-resolution TEM images of SnTe NCs viewed along [001] and [111] zone axes, correspondingly.

crystallinity of the SnTe NCs. Energy dispersive X-ray spectroscopy (EDX) showed nearly stoichiometric composition of the SnTe NCs (Figure S2).

The monodisperse SnTe NCs self-assembled into long-range ordered superlattices[18] upon slow drying relatively concentrated tetrachloroethylene (TCE) solutions of SnTe NCs by evaporating the solvent in a low-pressure chamber (∼3.2 kPa) at 50 °C (Figure 1a,b). The misalignment of the atomic lattice planes in the vertical rows of the SnTe NCs gives rise to rotational Moirè fringes seen for some NC columns in Figure 1b.

The size of the SnTe NCs can be controllably varied from 4.5 up to about 15 nm by adjusting the injection and growth temperatures and the concentration of OLA in the reaction mixture (Figure S3). Generally, the NC size increased with raising injection and growth temperatures; the optimal temperature range for synthesis of monodisperse SnTe NCs was observed between 90 and 150 °C. Lowering the concentration of the stabilizing agent (OLA) in the reaction mixture resulted in a decrease of the NC size (Figure S3). Since primary amines form strong complexes with Sn^{2+} ions, it is reasonable to expect that lower concentrations of OLA led to the
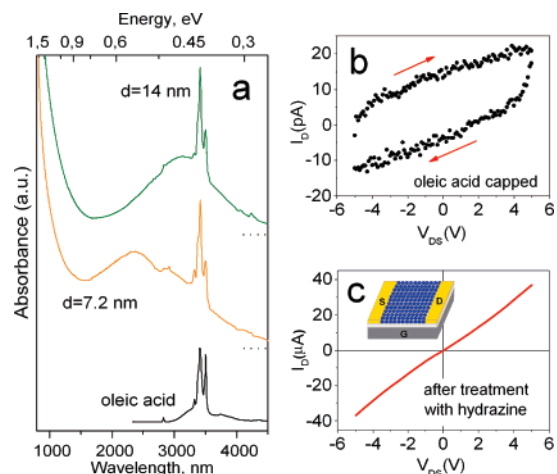
Figure 2. (a) IR absorption spectra of 7.2 and 14 nm SnTe NCs dispersed in CCl$_4$. The dotted lines indicate zero-absorption. Absorption spectrum of oleic acid is shown for comparison. The absorption bands at 0.36 eV originate from the oleate ligands bound to the NC surface. (b,c) $I-V$ curves for SnTe NC films: (b) as-prepared, oleic-acid capped 13 nm SnTe NCs and (c) film treated with 0.5 M solution of N$_2$H$_4$ in CH$_3$CN for 72 h. The inset shows schematics of the NC device.[17]

increase of the NC nucleation rate. With the larger number of nuclei formed, the less precursors were available for each growing SnTe NC yielding smaller particle size.[19] The same effect has been observed for the synthesis of PbS NCs.[1a]

The absorption spectra of the SnTe NCs showed pronounced peaks in the IR spectral range (Figure 2a). Since bulk SnTe is a direct gap semiconductor with a band structure similar to that of lead chalcogenides, we assigned these peaks to the 1S$_h$–1S$_e$ excitonic transitions. The sharp absorption lines around 3.4 μm, superimposed on each spectrum, represent the vibrational modes of the OA bound to the NC surface. The energy of the absorption peak could be varied by tuning the NC size owing to the quantum confinement effect. The values of the optical band gaps deduced from the absorption spectra are 0.39 and 0.54 eV for 14 and 7.2 nm SnTe NCs, respectively, making SnTe NCs an excellent material for mid-IR applications. The optical band gaps of SnTe NCs are close to the calculated optimal value (0.35 eV) for NC solar cells with carrier multiplication.[20] The excitonic peak can be further pushed into the IR by alloying SnTe NCs with lead telluride.[12]

To evaluate the potential of SnTe NCs for photovoltaic and thermoelectric applications we studied the charge transport in arrays of close-packed SnTe NCs. The films of as-synthesized oleic-acid capped SnTe nanocrystals showed low electrical conductivities of $\sim$10^{-10} S cm^{-1} (Figure 2b), caused by the large $\sim$1.5 nm interparticle spacing, maintained by the insulating oleic acid molecules.[5] The electronic conductivity, however, could be increased by at least 6 orders of magnitude by a treatment of the NC films with a 0.5 M solution of hydrazine in anhydrous acetonitrile[17] (Figures 2c and S4). Hydrazine molecules replaced bulky oleic acid ligands at the NC surface, reducing the interparticle spacing down to $\sim$0.4 nm, hence facilitating tunneling between the NCs.[5] The conductivity of SnTe NC films increased when we applied a positive bias to the back gate electrode (Figure S5), suggesting n-type

conductance in the arrays of N$_2$H$_4$-treated SnTe NCs. N$_2$H$_4$ could behave as an n-type surface transfer dopant for SnTe NCs.[5]

In summary, we have demonstrated the first solution-phase synthesis of monodisperse SnTe NCs extending the list of direct band gap semiconductor NCs. Our approach can be also adopted for SnS and SnSe NCs by replacing TOPTe for TOPSe or bis-(trimethylsilyl)sulfide (Figure S6). These materials can find use in near-IR and mid-IR optical applications, photovoltaic and thermo-electric devices. The environmentally benign tin chalcogenides could replace highly toxic lead chalcogenides nanocrystals in these and other applications.

Supporting Information Available: Experimental details, XRD, EDX, TEM, HRSEM, and electronic measurements data. This material is available free of charge via the Internet at http://pubs.acs.org.

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