Supporting Information for

Colloidal HgTe Nanocrystals with Widely Tunable Bandgap Energies: from Telecommunications to Molecular Vibrations

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Experimental details:

Synthesis of 3-4 nm HgTe nanocrystals (NCs) in aqueous solution. All reagents and solvents were of highest purity commercially available and were used as received. Deionized water was used throughout the experiments.

In a typical experiment, 150 mL of precursor solution were prepared by dissolving 2,72 mmol (1.65 g) of Hg(ClO₄)₂×3H₂O together with 7.88 mmol (0.89 g) of mercaptoethylamine (MEA) hydrochloride in deionized water and adjusting pH value to 4.1. The precursor solution was loaded into a 250-mL three-necked flask and was deaerated by bubbling with N₂ for 30 min. Subsequently, an appropriate amount of H₂Te gas was passed through the precursor solution under vigorous stirring. The final molar ratio of Hg²⁺/Te²⁻/RS⁻ was set to 1/0.5/2.9 giving a final concentration of HgTe NCs of about 12.1 mmol/L (referring to Te²⁻). For thioglycerol (TG) stabilizer, pH 9 is adjusted to 10.2.

Caution!!! Water-soluble salts of Hg²⁺ are highly toxic if in contact with skin or swallowed and extreme care must be taken when handling mercury perchlorate.

Electrochemical cell for generation of H_2Te gas. Here, H_2Te gas is produced via the electrochemical reduction of elemental tellurium in a strongly acidic solution ($Te^0 + 2 \bar{e} + 2H^+ \rightarrow H_2Te$ gas). The galvanostatic operation of the electrochemical cell follows well Faraday lows of electrolysis.

Therefore, the quantity of H₂Te gas can be easily calculated as follows: $v_{H_2Te}(mol) = \frac{I \cdot t \cdot \eta}{2F}$, where I

- current (A), *t* - time (s), η - current yield, *F*= 96485 s·A·mol⁻¹ - Faraday constant. Current yield was estimated to be 0.6 (at 0.5 A/cm² current densities and 293 K) based on gravimetric analysis and it is reproducible from electrode to electrode. The operation at 0.5 A was found to be most appropriate, because then the time of electrolysis (and thus the reaction time between Hg²⁺ and Te²⁻) for the above mentioned synthesis procedure is about 14.6 minutes and because no cooling of the cell is required.

The electrochemical cell is shown in Figure S1. It consists of a platinum anode and a tellurium cathode (S=1 cm²), immersed in 50%-sulfuric acid. Dry nitrogen serves as a carrier for the H₂Te. The level of H_2SO_4 should not be more than 1-2 mm above the Te cathode.

Caution! H_2 Te gas is highly toxic and any leakage from the equipment must be avoided, even if the experiments are carried out in an exhaust hood.

Growth of larger (4-12 nm) NCs. Since the variation of the nature of initial capping thiol-ligand does not show any significant effect on the nanocrystal size (as deduced from the luminescence experiments) we have promoted growth of larger particles by a post-synthetic heat-treatment under nitrogen atmosphere. Heating at 75-80°C provides a reasonably high growth rate for both, MEA- and TG-capped NCs as can be seen from evolution of luminescence peak positions with growth time (Figure S2). Ostwald ripening leads to disappearance of smaller particles and the growth of large ones with a significant broadening of the size-distribution. The latter can be improved by size-selective precipitation after the phase-transfer procedure described below.

Phase transfer from water to nonpolar organic solvents.

TG-capped HgTe NCs. 20-mL of the as-prepared solution of TG-capped HgTe NCs were placed into a vessel and a mixture of 10 mL of dodoecanethiol (DT) and 5 mL of acetone was added on top. The vessel was tightly closed and heated to 70°C for ca. 10 min. Afterwards, 2-3 mL of methanol was added in order to facilitate the separation of the emulsion into an aqueous phase on the bottom and an organic phase containing nanocrystals on top. The transfer efficiency is about 70-80%. The organic phase was extracted and washed several times with methanol giving a precipitate of DT-capped HgTe NCs. DT-capped HgTe were additionally purified by repetitive dissolving in hexane followed by precipitation with methanol and centrifugation of the resulting flocculate. Prior to the last precipitations, the HgTe NCs were filtered through a 0.2 μ m PTFE filter. Finally, particles were dried under vacuum and stored as a powder.

MEA-capped HgTe NCs. This procedure is essentially similar to that used for TG-capped HgTe NCs. The volume of added DT, however, can be as low as 1/8 of the aqueous phase and a complete phase transfer occurs after about 1 minute stirring at 70°C. Addition of few mL of acetone can further reduce transfer time to 10-20 s. Moreover, the MEA-capped HgTe NCs can also be transferred directly into diluted solution (1-2%) of DT in chloroform or toluene. In practice, it is very convenient to terminate growth of MEA-stabilized particles by injection of DT directly into the reaction flask at the growth temperature (75%).

DT-capped HgTe NCs are readily soluble in nonpolar organic solvents like chloroform, toluene, hexane etc. with a typical solubility of 5-30 mg/mL depending on the particular size and the solvent. These NCs remain highly luminescent after storing for at least several months at ambient conditions.

Size-selective precipitation. The size distribution of HgTe NCs after Ostwald ripening of about 20-30% can be narrowed to that of the initial colloid (10-15%) by means of size-selective precipitation. The dropwise addition of methanol into an intensively stirred toluene solution of DT-capped HgTe NCs till the appearance of turbidity (flocculation) and collection of the precipitate by centrifugation allows the separation of up to 6-8 fractions with narrower size distribution.

Preparation of HgTe NCs/PMMA films. These films were prepared by co-dissolving DT-capped HgTe NCs and PMMA in chloroform followed by spin- or drop-casting of the resultant blend solution onto Si substrates.

Relationship between stability and transferability of HgTe NCs. DT-capped HgTe NCs exhibit high stability in powdered form as well as in solutions. The stability of aqueous NCs strongly depends on the nature of hydrophilic thiol-stabilizer. The stability of the HgTe NCs colloids and their PL properties (decay of quantum efficiency and shift of the luminescence peak to longer wavelength) decrease in the following sequence: thioglycerol>thioglycolic acid>mercaptoethanol>L-cysteine>mercaptoethylamine. In the other hand, the transferability from the aqueous to the organic

phase increases in the same direction. The highest luminescence quantum efficiencies for asprepared HgTe NCs were found for TG- (30%) and MEA-stabilized (40%) NCs.

Optical characterization of HgTe NCs. For photoluminescence and optical absorption spectroscopy DT-capped HgTe NCs were dissolved in CCl₄ (spectroscopic grade) and placed into a quartz cuvette (1 cm optical path length). Linear absorption spectra were taken using a BOMEM DA8 Fourier transform infrared spectrometer operating from 10000 to 400 cm⁻¹. Photoluminescence was excited by InGaAs laser diode at 980 nm or by the second harmonic of a Nd:YVO₄ laser (532 nm), dispersed with a grating monochromator and acquired by an InSb detector. For the measurements of the luminescence quantum efficiencies in the Near-IR (1000-1800 nm) the intensities of the luminescence and of the excitation source was measured with a calibrated photodiode power-meter. The room-angle (given by the first collection lens), the reflectivity at each interface and the transmittance of each optical element (lenses, cuvette) were taken into account for determination of the total emitted intensity. For the samples emitting at wavelengths longer than 1800 nm, the quantum efficiencies were calculated by comparing their integrated intensities with those of NCs emitting at shorter wavelength, taking into account the spectral response of the monochromator and InSb detector.

Structural characterization of HgTe NCs. X-ray diffraction (XRD) spectra were collected on SEIFERT XRD3003 diffractometer operating in the Bragg configuration using Cu K α radiation (1.5406 Å). The samples for XRD were prepared by embedding HgTe NCs into a PMMA matrix at concentration of 5-10 % (w/w), in order to prevent toxicity risks associated with handling of powdered samples. Such samples act as a diluted powder of HgTe NCs. The sizes of particles were obtained on the basis of Scherrer equation using fwhm values of (111) peak.

Samples for TEM were prepared by placing 1-2 µL of a diluted (0.1 mg/mL) HgTe NCs solution in toluene onto a carbon-coated (5 nm) copper grid. Excess of solvent was removed after 10 s, samples were dried and kept in vacuum for several hours prior to measurements. The TEM pictures were obtained using JEOL 2011 FasTEM microscope operating at an accelerated voltage of 200 kV.



Figure S1. Compact electrochemical cell for generation of H₂Te gas.



Figure S2. Temporal evolution of the luminescence peaks for different thiol-capping molecules (measured after phase-transfer).



Figure S3. Particle-size-tunable photoluminescence from HgTe NCs embedded in a polymethylmethacrylate (PMMA). Arrow indicates overlap of NCs emission with C-H stretching absorption band of the PMMA.



Figure S4. High-resolution TEM image of a HgTe nanocrystal with stacking faults.



Figure S5. Selected area electron diffraction pattern of ~ 50 HgTe NCs indicates their high crystallinity. The indexing of the dot-rings confirms the zinc-blend crystal structure of the HgTe NCs.